

Leaching of Phase II Mercury Control Technology By-products

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ABSTRACT

The U.S. EPA has issued a final regulation for control of mercury from coal-fired power plants. An NETL research, development and demonstration program under DOE/Fossil Energy Innovations for Existing Plants is directed toward the improvement of the performance and economics of mercury control from coal-fired plants. The current Phase II of the RD&D program emphasizes the evaluation of performance and cost of control technologies through slip-stream and full scale field testing while continuing the development of novel concepts. One of the concerns of the NETL program is the fate of the captured flue gas mercury which is transferred to the condensed phase by-product stream. These adulterated by-products, both ashes and FGD material, represent the greatest challenge to the DOE goal of increased utilization of by-products. The degree of stability of capture by-products and their potential for release of mercury can have a large economic impact on material sales or the approach to disposal. One of the considerations for mercury control technology is the potential trade-off between effective but temporary mercury capture and less effective but more permanent sequestration. As part of a greater characterization effort of Phase II facility baseline and control technology sample pairs, NETL in-house laboratories have performed aqueous leaching procedures on a select subset of the available sample pairs. This report describes batch leaching results for mercury, arsenic, and selenium.

1. Introduction

The U.S. EPA has issued a final regulation for control of mercury from coal-fired power plants. The Clean Air Mercury Rule (CAMR) establishes a phased in schedule to cap emissions of mercury from combustion flue gas. Initially reductions are based on the co-benefit associated with compliance with the more

broadly focused Clean Air Interstate Rule, and second phase reductions are targeted specifically on adoption of mercury control technologies. The potential of the promulgation of these regulations was recognized by DOE/NETL in the early 1990s, when the comprehensive R&D program focused on mercury was established. The collaborative effort involving power producers, the Electric Power Research Institute, the US EPA, agencies of state and local governments, and academic researchers laid a sound foundation for the current program. An NETL research, development and demonstration program under DOE/ Fossil Energy Innovations for Existing Plants is directed toward the improvement of the performance and economics of mercury control from coal-fired power plants. The three principal forms of flue gas mercury are particulate-bound, oxidized, and elemental. For the earlier CAMR requirements, particulate control devices can capture the particle-bound form, oxidized mercury can be removed by FGD systems, and the elusive elemental form can be converted by the SCR process for NO_x control to the oxidized form, and subsequently removed by an FGD absorber. For the much lower limits of mercury release allowed by the final emissions cap of CAMR, the most tested approach involves the injection of activated carbon. Phase I of the program was directed toward characterizing emissions and performing short duration proof-of-concept tests on laboratory, bench, and pilot scales. The on-going Phase II of the RD&D program shifts emphasis to the evaluation of performance and cost of control technologies through slip-stream and full scale field testing while continuing the development of novel concepts at the bench and pilot scale. Test results have indicated that mercury capture is less effective for plants that burn lower rank coals. This finding has been linked to a higher percentage of elemental mercury from lower rank coal use and a lower amount of chlorine in these fuels. Phase II tests have a particular emphasis on lower rank coals and coal blends. The advanced sorbents include activated carbons that contain added halogens.

The NETL program is also concerned with the fate of mercury in capture technology by-products. Any captured flue gas mercury will be shifted to a condensed phase by-product stream. A goal of DOE is to not only maintain but also increase the utilization of coal use by-products. Some advanced capture technologies are designed to remove most fly ash before the introduction of a capture sorbent. Nonetheless, the portion of the solid by-products containing mercury capture additives will represent a significant volume of material as control technologies are adopted nationwide. It is these adulterated byproducts, along with FGD material, that represent the greatest challenge to increased by-product utilization and the greatest economic impact with respect to lost sales of ash and potential costs of disposal. An important part of this issue is the potential of future release of mercury from the capture by-products. One of the considerations for commercialization of control technologies is the potential trade-off between effective but temporary mercury capture and less effective but more permanent sequestration. To evaluate the various control technologies as applied to different coals and different power facilities throughout the country, DOE/NETL has funded a selected contractor to perform an extensive

investigation of the conditions of and extent of release of mercury from relevant CUB under a number of utilization and disposal scenarios. Samples pairs from baseline and mercury capture conditions have been collected from a number of active facilities. Among the evaluations being performed by the contractor is the Synthetic Precipitation Leaching Procedure (SPLP, EPA Method 1312), which has been modified to provide for longer term leaching of samples, up to 30 days of exposure to the leaching solution. The DOE/NETL on-site laboratories performed the modified SPLP [1], the NETL Serial Batch Leaching Procedure (SBLP) [2], and NETL Column Leaching [3] on a select number of sample pairs. Currently, many of the leaching tests described in the published Integrated Framework Evaluation [4] are being applied to these sample pairs.

The altered character of a facility's by-products as a result of the addition of mercury control technology is expected to disrupt traditional and emerging utilization efforts and has the potential to increase the cost of disposal. Evaluations of the stability of the new by-product streams are necessary. The results will serve to assure generators, potential users, disposal managers, regulators and RD&D program officials of the safety and effectiveness of the proposed control strategies. The approach adopted by this project is directed toward the evaluation of the stability of sequestered mercury and other trace elements in Phase II ash samples with respect to aqueous leaching. The potential for release of halogens, important additives to the activated carbon of many experimental mercury control technologies, is also being monitored. Different environmental scenarios for the new by-product streams require different information from leaching tests. There is sparse data on the release of mercury and other species from mercury control by-products. What limited data is available supports the stability of mercury in terms of it being retained in the ash mixture. The generation of additional data from multiple sources showing the stability of mercury capture will aid utilization efforts of the new byproducts and minimize environmental concerns regarding handling the material.

2. Technical Approach

The laboratory-scale leaching work at NETL provides information for CUB producers, handlers and DOE program officials to assist in the determination of the environmental compatibility of CUB with various utilization or disposal scenarios. The leaching techniques applied focus on the potential release of ash components into surface and groundwater. In these studies, samples of solid phase substrates were extracted with leachants which can dissolve or mobilize constituents of the solid and mimic some aspect of a particular environment. The leaching techniques in the current project can be classified into either the batch or continuous category, based on the mode of contact by the leachant. Batch leaching tests are the most common and many analyses are based on single or multiple batch tests. Batch techniques quickly provide information on metals release at a set pH and liquid-to-solid ratio. Common examples include the TCLP [5], which was developed to mimic co-disposal of wastes in municipal

landfills, and SPLP, which was designed to simulate the action of acidic rainfall. More recently, the NETL sequential leaching procedure has been developed to provide leaching data at several pH values and liquid-to-solid ratios. This protocol can properly be classified as a serial batch method due to the sequential nature of the component steps. The NETL method is best suited for CUB exposure to a natural setting that includes exposure to flowing water and replenishment of the surrounding aqueous environment. In such a scenario, L/S values will increase over time, and highly soluble species will wash out. The dominant influence of major ash components on the pH conditions of the immediate environment of a CUB will be tempered over time, as the leaching conditions shift toward those of the local aqueous media. Thus, at later periods of longer term leaching, both the pH of the leaching media and the material being leached are different. This change in ash composition means that the solvating and precipitating processes resulting from interactions between components of the material being leached can also change. Under less dynamic conditions, where the aqueous media is not removing soluble species, other environmental influences and mineralization processes may be more significant. For such conditions, sequential leaching may be less important, and longer term exposure to a constant leaching fluid, such as described in the Synthetic Groundwater procedure [6] may be more important. The NETL method is based on a general scheme of the International Ash Working Group [7], derived from extensive work of the Netherlands Energy Research Foundation [8], after further development by the European Standardization Organization [9]. The U.S. EPA has stated its support of the adoption of the Integrated Framework approach and its 3-Tier method for the leaching of CUB and other materials. The NETL SBLP includes procedural elements that have some similarities to what would be classified as Tier 1 or Tier 2A within the Integrated Framework method.

The NETL By-product Utilization Team and the specific researchers responsible for the on-site technical activities in this work have demonstrated experience in the characterization of release potential of species in coal utilization by-products. The extensive column leaching data has been the basis for published work for a number of years. Analyses are routinely performed for mercury and a large number of other elements on leachates from both the column runs and the batch leaching tests. Column work has examined a wide variety of by-products, and recent column leaching has been performed on samples derived from ash from high mercury coal, a Phase I by-product, and ash from on-site activated carbon injection tests. The acetic acid leachant has been especially effective at leaching mercury. The batch leaching has evaluated the release of metals from a number of Eastern fly ashes, and a report on this work has been submitted to a peer-review journal. The NETL method and several other approaches have been applied to samples in a collaborative method comparison study that includes coal ash from Eastern and Western U.S. A manuscript describing this work is in preparation. Through this effort, the NETL laboratories gained some experience using leaching procedures of the Tier 1 and Tier 2B class within the Integrated Framework approach. These procedures are currently being used to

characterize Phase II Hg control sample pairs with this protocol. For many samples analyzed prior to the current work, generated by the various parts of the NETL batch and other methods, mercury release has been below detection.

A standardized approach to acquiring toxic metals release information from solids under aqueous conditions has not yet been established throughout the regulatory, commercial, and research community. The SPLP remains an evaluation method for material on the Federal level and in the regulations of many states. An expanded version of the SPLP and NETL's batch leaching procedure were applied to a select subset of Phase II samples. This effort has examined samples over a spectrum of leaching conditions that include various leachants, a range of pH environments, and different liquid to solid ratios and time periods. Leachates have been analyzed for mercury, halogens, and a list of other elements, including arsenic and selenium. The discussion of this report will focus on mercury release from four sample pairs, comparing the retention of Hg by control technology samples to the retention of Hg by the corresponding baseline ash. Results for As and Se from the batch methods have also been included. For this report, replicate sets of data from four discrete leaching steps from the Integrated Framework Tier 2B approach for one of the sample pairs were used for comparative purposes. These data allow for a contrast in results based on leaching time or sequential vs. non-sequential batch protocols. This data is referred to as "3T" (for 3-Tier) in Figures 5, 7, and 12.

3. Experimental

Samples were shipped from the test facility to the contractor. The contractor performed a homogenization of the sample, thereby ensuring that identical sub-samples were examined in each of their evaluations. One of these sub-samples was sent to NETL for the several leaching tests.

The NETL Serial Batch method consists of an availability portion that estimates the amount of material leachable over a range of set pH values, and a long term simulation, which leaches with DI water over a range of liquid to solid (L/S) ratios, the volume of leaching solution in liters to mass of ash in kilograms, L/kg, or mL/g, which were the actual units of measurement. For the typical, highly alkaline material, the availability test was begun on 9 g of ash with 450 mL of DI water, run at its natural, uncontrolled pH for 2 hours. After pressure filtration (0.45um pore filter), the filtrate was isolated for analysis, and the filter and residue were returned to the extraction vessel. An additional 450 mL of DI water was added, and the pH was then maintained at a setting of 8 with an automatic titrator using dilute nitric acid for 3 hours. The filtration and subsequent steps were repeated at pH 4 for 2 hours, followed by pH 2 for 2 hours, generating 4 leachate samples. One of the received sample pairs consisted of acidic material, and an alternate set of pH values has been established for the availability evaluation of such materials. These conditions were two separate sequences: natural pH followed by pH 8; and natural pH, pH 4, and pH 2.

The long term simulation sequence was performed on 45 g of ash and was begun with 90 mL of DI water, providing an L/S ratio of 2. The mixture was placed on a bottle roller for 6 hours. As in the availability portion, the mixture was pressure filtered, an analysis sample was generated, and the filter and residue were returned to the leaching vessel. A volume of 180 mL of DI water was added (L/S=8), and the mixture was rolled for 18 hours. This process was repeated at L/S= 10 for 24 hours. In a separate leaching, a 10 g sample was leached with 1 liter of DI water (L/S=100). A total of four leachates per sample replicate were generated from this L/S part of the method.

The SPLP, EPA Method 1312, was modified, such that aliquots were taken for analysis at 18 hours, 14 days, and 30 days, instead of only the 18 hour duration of the standard procedure. A 100 g sample was mixed with 2 L of DI water which had been pre-adjusted to an acidic pH with a 60:40 mixture of sulfuric: nitric acids. The method has two options for this pH, and the slightly more aggressive pH 4.2 was selected, which is typically used for Eastern U.S. applications, instead of the Western pH 5.0 solution. For the six highly alkaline CUBs, the pH 4.2 solution did not significantly alter the highly alkaline pH that was obtained when these materials were mixed with only DI water. By this method, the mixture was agitated in an end-over-end tumbler.

The parameters of the selected Tier 2B method components of the Integrated Framework Evaluation which provided data included in this report are that 40 g samples were tumbled end-over-end for 24 hours with 400 mL DI water (L/S=10), to which volumes of nitric acid had been added. The 24 hr duration is a modification made by the authors of this method for materials such as fly ash; the earlier published version of this protocol uses 48 hr leaching times. The acid volumes were determined by a titration pretest to target a broad range of pH values. The method also includes a series of L/S ratios in DI water similarly agitated. The data selected for this report were from those replicate sets of leaching steps in this method whose average final pH values or L/S values most closely matched the conditions of the NETL SBLP. For that purpose, the data from this method, averages of 3 replicates and included on Figs. 5, 7, and 12, are the leachates whose final pH values equaled 8 (pH 8-3T) and equaled 5 (pH 5-3T) and runs at L/S=2 (L/S 2-3T) and =10 (L/S 10-3T). The use of selected data from the Integrated Framework method was for comparative purposes only, and is not intended to imply that the method, including data evaluation, as fully described and applied by its authors or sponsors was followed in its entirety, or that the entire method in its full form was applied to these samples.

Raw ash samples were analyzed following preparation by microwave digestion. Leachates were analyzed neat or diluted as necessary. All samples were analyzed for a wide spectrum of elements, from arsenic to zinc, by inductively coupled plasma (ICP)/optical emission spectroscopy (Perkin Elmer Optima 3000 ICP-OES). Mercury was analyzed for by cold vapor atomic fluorescence

(CETAC Quick Trace M8000). An ICP/mass spectrometer has been obtained (Perkin-Elmer ELAN II ICP-MS), and the enhanced sensitivity of this instrument was available for some leachate analyses where species of interest were below detection by the optical technique. The detection of halogens, especially chlorine and bromine was performed by ion chromatography. Results from these anion analyses are not included in this report.

4. Results and Discussion

4.1. Batch leaching - mercury

Batch leaching data on mercury release from the four pairs of samples has been reduced to Figures 1-5. The four pairs of baseline and control technology materials were evaluated in terms of how much less mercury was released by a mercury-capture technology ash (Hg control sample) than was released by a facility's corresponding baseline-operation ash under various aqueous leaching conditions. It is not the initial capture of Hg from flue gas, but rather how effectively this Hg is retained in aqueous environments that is the primary subject of this report. All capture technology ashes had higher Hg contents than the corresponding facility baseline material. For Figs. 1-4, these materials are designated by MCT (mercury capture/control technology), a sample number, and B (baseline) or C (capture or control). This designation is shortened to 1B, 2C, etc., in some of the later discussion and on Fig. 5. Sample pairs are 1&2, 3&4, 5&6, and 7&8, and measured Hg values are given below in μg Hg per kg ash (ppb Hg):

MCT-1-B	2-C	MCT-3-B	4-C	MCT-5-B	6-C	MCT-7-B	8-C
179	1348	2.18	485	98.8	221	48.3	199

Further descriptions of the samples are provided below:

<u>Ash</u>	<u>Coal</u>	<u>Pollution control</u>	<u>Mercury control</u>
MCT-1-B, 2-C	Sub-bit	Spray dryer/fabric filter	Br-activated carbon
MCT-3-B, 4-C	Lignite	Spray dryer/fabric filter	Activated carbon + sorbent
MCT-5-B, 6-C	Lignite	Cold-side ESP	Activated carbon + sorbent
MCT-7-B, 8-C	Bit	Hot-side ESP	H-PAC

In some cases, the Hg content of the capture ash is much greater than for the baseline sample from a technology pair. In those pairs, equivalent fractions of Hg content release represent a significant net stability with respect to aqueous leaching for the capture material over the baseline sample.

The Phase II total release data on Fig. 1 shows the cumulative release of Hg after the third step of the NETL SBLP long-term simulation sequence (L/S series), which is L/S=20. These data were derived from the average of three replicates of the leachates from the cumulative L/S series of L/S=2, L/S=10 (2+8) and L/S=20 (2+8+10). This leaching test provides cumulative release data for sample constituents as the bulk sample is exposed to a flow of water over time, and can be used as the basis for relative release rates. The leachate samples were analyzed for mercury by cold vapor atomic fluorescence, and this soluble concentration value was converted to μg mercury per kg of original ash leached for the Fig. 1 data. Fig. 2 uses the original concentration values. The amount of mercury in the leachate, in μg per kg of starting ash, divided by the total mercury content of the ash is the “fraction of ash mercury released,” shown on Figs. 3 and 4. The logarithmic scale of the Y-axes of Figs. 1-4 is needed to demonstrate the large range of mercury retention of the baseline and capture technology by-products evaluated. The next data on Fig. 1 are results after the single step runs at L/S=100 and the SPLP sampling at 18 hrs, 14 days, and 30 days. Also shown are cumulative data after the second availability step of pH=8 (pH=11, then 8 for the alkaline MCT-1 – MCT-6 and pH= 4.5, then 8 for the acidic MCT-7&8) and cumulative data at the terminal pH=2 step for the alkaline 11,8,4,2 series or the acidic 4.5,4,2 sequence. For the six alkaline ashes, pH 11 is used to refer to the natural pH step, actually pH=11-12. The pH 4.5 step is the natural pH step of the two acidic ashes, actually pH=4-4.5. The legend of Fig.1 also provides the Hg content in μg per kg of the raw, as-received ashes that was provided above. On figures 1-4, the absence of a data point means that all Hg levels of all replicates of leachates from either the single step runs or the cumulative data up to the point indicated were below analytical detection. Where points are shown, data is the average of three replicates. Where only some replicates were below detection, these values were considered to be zero for averaging purposes.

For all Fig. 1 data, the release of Hg was small compared to ash Hg content. The Hg content of 7B was 2nd lowest among baseline ashes and that of 8C was lowest among capture materials. The Hg release from these ashes, where detectable, is generally lowest as well. The 30 day SPLP results show little difference in total Hg release within pairs, although ash Hg content is greater in control samples by factors of 7.5, 222, and 2.2 for the MCT 1&2, 3&4, and 5&6 pairs, respectively, and by a factor of 4 for the 7&8 pair. The 7&8 pair did not provide measurable Hg in their leachates from this leaching step. Thus, a net retention of Hg is being observed over the 30 day duration of this leaching for the control technology members of at least the alkaline ash pairs. Evidence of control sample stability with respect to Hg release is also shown by the 14 day SPLP data for the 1-2, 3-4, and 7-8 pairs, and the 18 hr results for the 1-2 set.

The L/S=20 data of Fig. 1 shows enhanced Hg stability for the control sample over the baseline ash in the 3-4 pair especially and for the 5-6 pair to a slight extent. At the near neutral pH=8 stage, 3-4 and 5-6 pairs again show control samples with lower Hg release levels than corresponding baseline ashes. At pH

2, 6C shows more stability with respect to aqueous release of Hg than its baseline 5B than is evident from the other pairs. The stability of 4C relative to 3B is also evident when the respective Hg content of these ashes is taken into account.

The leachate Hg concentrations for the single run steps and the initial steps of leaching sequences are shown in Fig. 2. The neutral pH (pH Nat) level is 11-12 for samples 1B through 6C, and this pH is 4-4.5 for 7B and 8C. At L/S=2, the enhanced aqueous Hg stability of a capture sample over the corresponding baseline ash is most dramatic for 4C and notable for 6C. At the availability natural pH step (where L/S=50), samples 4C, 6C, and 8C all show lower Hg concentrations than their baseline counterparts, in spite of higher Hg contents in the respective capture ashes. The SPLP data is complete, but the 2C data is nearly the same as and is obscured by the 4C result, while the 5B value is identical to and covers the 3B data. The similar values of Hg concentrations within pairs, best shown in the SPLP 30 day runs, indicates a general net sequestration of Hg for the alkaline control ashes under these conditions. The below-detection values of the 7-8 pair do not allow conclusive evaluations from this test.

The fraction of contained Hg that was released is shown in the leaching time and the L/S ratio data comparisons depicted on Fig. 3. As on Fig. 2, all data shown are from leaching that occurred at or very near the natural pH of an ash. Missing data on Fig. 3 means results were below detection. The L/S 50 values are the initial, natural pH data from the availability sequence. From this test, the 2C release fraction is greater than that of 1B. The ratio of Hg contents for 2C to 1B is greater than the ratio of their release fraction. From this perspective, the 2C control material provided a slight net retention of Hg. The other data sets all demonstrate a clear advantage of Hg retention in the control sample from this test, and are all the more effective, considering that their control ashes also have higher Hg contents than their baseline ashes. In the L/S sequence of Fig. 3, the fraction of Hg released for 1B was below detection at L/S 2, but was greater than 2C at larger L/S values, which are also longer times. The fractional advantage of Hg retention for 2C was maintained throughout the SPLP sequence shown on Fig. 3. In other cases on Fig. 3 where both 1B and 2C were detectable, sample 2C showed a clear retention of Hg to a greater extent than 1B. Throughout Fig. 3, the much higher Hg content of 4C over 3B, combined with the much enhanced ability of 4C over 3B to retain its Hg under various time and L/S conditions, produced the most significant results. The 6C capture ash demonstrated its advantage in Hg retention over the baseline 5B throughout the L/S runs, including at L/S=100, where dilution effects may contribute to most other ash results being below detection. In the SPLP runs, the advantage of Hg retention for 6C over 5B is clear only at 30 days. For the earlier 18 hr and 14 day runs, leachate concentrations of 5B and 6C are similar, and the fractions of Hg content leached represent the higher Hg content of 6C. The Hg release from both 7B

and 8C are low or below detection for data in Fig. 3, and no clear conclusions can be drawn from these mildly acidic leachings for this sample pair.

The fraction of ash Hg released as a function of leaching step pH is shown on Fig. 4. All data are from the NETL SBLP availability sequences, and trend lines are included. The experimental sequences follow the left-to-right depictions. Because data are cumulative, the direction of trend lines can be flat or upward, but cannot go down. The data are grouped into the alkaline ash availability sequence of descending pH (Alk) on the left, and the ascending pH sequence of natural pH to pH=8 for acidic material (Ac-a) and the descending pH sequence of natural to pH=4 to pH=2, also for acidic material (Ac-b). The Ac-a and Ac-b trends are for the hollow data points of the 7&8 ash pair, and the three groupings are indicated on the X-axis. The 5B and 6C trends are both flat, indicating that leachable Hg was released only at the initial, alkaline, natural pH step. A clear advantage of Hg retention was demonstrated by the capture material over the baseline ash from this test. The greater retention of Hg by capture sample 4C over its baseline 3B ash is most evident at the initial alkaline step. This retention advantage is diminished by the end of the pH sequence but is still large, especially considering the greater Hg content of the 4C ash. A steep rise in the trend line of 4C on this figure is shown from pH=8 to pH=4, and the 1B sample also shows a rise in this region. At the initial, natural pH step, a greater fraction of contained Hg and a greater amount of Hg was released from the 2C ash relative to 1B. This result is also shown by the L/S 50 data of Fig. 3 and the pH Nat data of Fig. 2. As the sequence for 1B and 2C on Fig. 4 progresses and pH drops, the fractional difference for this pair decreases. For the acidic 7B and 8C ashes, the fraction of Hg released trended upward sharply from the natural pH to pH=8. Some of the advantage of Hg retention by 8C decreased at this near-neutral pH. An upward trending was also observed for 8C in the descending pH sequence, but here all data for 7B were below detection.

The 1-B and 2-C data are grouped on Fig. 5. The Tier 2B leachate data continue to support the slight net retention of Hg by this control ash sample relative to the baseline material. For the L/S 2 and the L/S 2-3T, the experimental scale is nearly identical. The differences are that the former sample was on a roller for 6 hrs and the latter was tumbled for 24 hrs. The mixed result was that the Tier 2B baseline leachate had detectable Hg, where the SBLP baseline Hg was below detection, and the Tier 2B control leachate contained less Hg. At L/S 10, the baseline results from the 2 methods were much closer, while the control sample data were further apart. The procedures were different for these tests, since the L/S 10-3T leachate was from a discrete experiment, whereas the L/S 10 data is a cumulative sum of the L/S 2 plus a subsequent L/S 8 step of the same ash particles. Still, the total leaching time of each method at L/S 10 was 24 hrs. From these data, larger amounts of Hg were reported for both baseline and control ashes from the SBLP. The comparison of data from the pH 8 (SBLP) and the pH 8-3T (Tier 2B) show the latter leaching to have released almost as much Hg from the baseline sample, but clearly less Hg from the Hg capture ash. For

these data sets, the SBLP result is a cumulative sum of a natural pH (near 11) run and a leaching maintained at pH 8. The Tier 2B data are from the run replicates targeting pH 6. The final pH values from both approaches were 7.5-8. The SBLP natural run contributed most of the released Hg shown at pH 8 and the later steps of the sequence. Total leaching times from the SBLP after pH values of 8, 4, and 2 were 5 hrs, 7 hrs, and 9 hrs respectively, while all Tier 2B steps shown were run for 24 hrs. The Tier 2B method pH steps generated data at L/S 10, whereas the cumulative SBLP method contained pH steps each run at L/S 50, producing cumulative L/S values of 100, 150, and 200 at the reported pH levels of 8, 4, and 2, respectively. The pH 5-3T data were from the lowest pH run of the Tier 2B set, targeting pH 3. These Hg release data were very similar to the control sample Hg data from the SBLP. The pH 5-3T baseline Hg result is above all other Hg release findings for this ash pair. Based on the Hg results of Fig. 5, the 24 hr leaching times are not required for this ash pair, and the fine size (<300 μm) may be allowing shorter leaching times to be sufficiently effective for this screening purpose. Future use of the Tier 2B method at NETL will produce results at lower final pH values, extending to pH<2. This modification is in agreement with current practice of the method's designers.

The pH 8 and pH 2 data of Fig. 1, the availability test pH Nat data of Fig. 2, the L/S 50 data, which is from the same test, of Fig. 3, the SPLP values on each of these figures, and the full set of availability pH data on Fig. 4, allow for comparisons across all of these figures. The baseline data for Hg are by definition what would be present in the control ashes if the control technology was not applied. Therefore the full difference in amounts of Hg found in the control samples is the added and captured Hg. If the control samples were completely ineffective at retaining their captured Hg under the described leaching conditions, all of it would be released by these tests. Clearly, however, all four tested materials do retain captured Hg. Under the worst conditions observed, some cases for ashes 2C and 8C, Hg is released to an extent proportional to Hg content, which still represents a net retention of captured Hg. Under the best of cases, some results for 4C and 6C, not only is captured Hg retained, but Hg that normally would be released from the baseline ash is retained as well. From this perspective, Hg is being diverted from atmospheric release in stack gases and is being effectively sequestered in the resultant control technology ashes for the materials and conditions examined.

4.2. Batch leaching – arsenic

The arsenic content of the 8 CUBs ranged from 28.3 – 46.7ppm by weight. The control samples of pairs 3B/4C, 5B/6C, and 7B/8C contained 13%, 36%, and 4 % more arsenic, respectively, than the baseline ash, while the 2C ash had 2% less As than 1B. The leachate As levels were frequently below the detection levels of 7-25 ug/L. Samples 1B and 6C only reported As from the pH 2 step of the NETL

SBLP alkaline ash availability sequence and the 1B results from the Tier 2B leaching, and only the Tier 2B runs at L/S 10 generated leachates of 2C with detectable As. Leachates of samples 3B, 4C, and 5B only reported As in the alkaline availability steps at pH 8 and pH 2. Samples 7B and 8C had detectable As in the SBLP acidic availability steps of pH2 and pH8. Ash 7B also reported As from the L/S=2 step and the SPLP 18 hr leachates, while the 8C leachate from the SPLP 14 day step showed As. The general absence of detectable of As in natural pH leachates precludes much of the discussion of time-dependent behavior. The fraction of ash As released by the availability tests is shown on Fig. 6, and all detectable As results from leaching 1B and 2C are shown on Fig. 7. On Fig.6, the 3B data is obscured by and nearly identical to the 4C results. The alkaline pH 4 data represents the cumulative nature of this leaching sequence only, since no additional As was released at this pH for the alkaline or the acidic ashes in their pH sequences. The pH 8 leachates show behavior consistent with an elevated solubility of oxyanionic species at near neutral pH over their natural pH results. Mildly acidic leachings produced no detectable As except for the Tier 2B results, but a much more acidic environment released about 20-40% of contained As for samples 3-8. A net retention of As is shown by the 4C and 6C samples over their baseline ashes for the pH conditions studied over the depicted conditions. The 7B/8C data are less dramatic, and the 1B point on Fig. 6 near the detection levels is inconclusive. The limited data on Fig. 7 weakly supports greater As release from the Hg control sample.

4.3. Batch leaching – selenium

The batch leaching results for selenium are summarized on Figures 8-12, following the format used on Fig. 1-5 for Hg. Due to the solubility of Se species in alkaline media, Se release was observed from DI water leachings of the 6 alkaline ashes, including the availability natural pH step. For the acidic ashes, where all DI water leachings, including the availability natural pH steps are mildly acidic, Se detection was rare. This metal was reported from the pH=8 step for all ashes except 6C and 7B, no pH=4 steps, and at pH=2 for only 3B and 4C. The Se data shown for the 1B/2C and 5B/6C pairs at these lower pH levels on Figs. 8, 11, and 12 are from the cumulative summing operation. The discrete Tier 2B leaching steps for 1B and 2C produced data for all conditions reported on Fig. 12. As indicated in the legend of Fig. 8, the Se control samples contained more Se than their baseline counterparts. These increased contents of Se are relatively much smaller percentages than was observed for the Hg content comparisons of control to baseline samples (Fig. 1). Selenium was not detected in the 7B raw ash sample (D.L. 15000 ug/kg), nor in the post-leaching ash analyses (D.L. 3000 ug/kg), where residual insoluble species are more concentrated. Therefore, there are no entries for 7B on Figs. 10 and 11, although Se release is shown for 7B on Figs. 8 and 9.

The total release of Se from individual and cumulative leaching steps is shown on Fig. 8. At the terminal L/S 20 step of that sequence, the 4C ash shows a

small net Se retention, the 6C sample shows much less of an advantage, and the 2C ash data implies a potential for an increased release of Se, all relative to their baseline counterparts. The dilution at L/S 100 may be the cause of limited data from this step. From the SPLP at 18 hrs, only 4C again shows a clear net Se retention over its baseline ash. At 30 days, the SPLP data trends are similar to the 18 hr results for the 1-2 and 3-4 pairs. At pH 8, where an oxyanionic form of Se can be a significant contributor to this element's solubility, release values are generally higher than at the prior natural pH levels of this figure. Ash 4C released half of its additional Se content relative to 3B by this step, a trend continued from the initial natural pH leaching step. By pH 2, nearly all of the additional Se of 4C was released. The 6C sample was effective at retaining Se relative to 5B under the near neutral and acidic conditions, while the 2C ash demonstrated only a slight retention of Se.

The leachate concentrations of Se under natural pH conditions are shown on Fig. 9. The data presented are all single steps or the first of a sequence. The 6C sample provides the best evidence for net Se retention in data pairs, and this finding is demonstrated over all conditions shown. For reference, the Federal Drinking Water standard for Se = 50 ug/L (www.epa.gov/safewater/contaminants). This contaminant level is exceeded by some of the non-attenuated conditions in this study, demonstrating the ready solubility of some Se species.

The effects of increasing liquid to solid ratio and of increasing leaching time are shown on Fig. 10. The L/S 2-10-20 sequence incorporates both of these features, and in cumulative data that can remain level but cannot decrease. There is considerable overlap of data points, with the 18 hr SPLP 4C value eclipsing the 2C and 3B data, and the 30 day SPLP 1B data covered by the 4C value. There is a general upward trend in fraction of Se released with increasing L/S, and a more level effect with time. Due to the sampling technique used, the SPLP values for L/S decrease with time from 20 to 19 to 18.

The Se fractions released with respect to pH are shown as cumulative sequences on Fig. 11. Again, the trend lines can remain level but cannot go down. The behavior of additional Se release as the pH dropped from 11 (actually 11-12) to 8 is clearly shown for all alkaline ashes except 6C. This result is what can be expected over time in those environmental scenarios where the alkalinity caused by major components of the ash are gradually washed out or neutralized. The 3-4 sample pair shows a second Se release when the pH is further dropped from 4 to 2. The 6C sample most clearly shows its retention of Se relative to its baseline ash.

On Fig. 12, the increased leaching time of 24 vs. 6 hrs for the L/S 2-3T over the SBLP L/S 2 leachate may have caused the release of more Se in this former method's 2C sample, but the same trend was not as evident for the 1B leachate. Where total leaching times are the same, the L/S 10-3T results are only slightly

higher than the SBLP cumulative L/S findings. The pH 8-3T values are near but lower and the pH 5-3T values are near or higher than the SBLP pH data on Fig. 12. The additional leaching times for these Tier 2B pH-effect leachings do not show by themselves a significant influence in Se release.

5. Summary

Mercury - The results of this study are very promising for mercury capture. Not only have the mercury control technologies demonstrated capture of mercury that would otherwise be released into the environment at the plant site, but the mercury has generally been shown to be retained in the control technology by-products under conditions of laboratory leaching tests. For some of these materials, the tests performed in this study show these control technology ashes, in spite of their higher Hg content, to be environmentally more stable with respect to Hg release than the corresponding baseline ashes of lower Hg content.

Arsenic - Under the most acidic conditions tested, arsenic release from ashes with or without Hg control approached a level of concern with respect to drinking water standards. These levels can be expected to become extremely attenuated under most environmental conditions. The type of results provided by the leaching tests in this study can provide an indication of which materials most warrant monitoring for As release, if they are to be exposed to severely acidic conditions.

Selenium - The solubility of Se species was especially evident under circum neutral conditions. Some laboratory leachates approached or exceeded drinking water standards for Se concentration. For utilization or disposal scenarios where there is aqueous flow and replenishment, more neutral pH levels and higher Se solubilities can be achieved, but these very environmental conditions will attenuate Se concentrations.

The several Hg control technologies represented by the samples tested in this study were developed for and are effective at Hg capture and demonstrate retention of this metal with respect to the variety of leaching tests in this study. These materials are not nearly so effective at capture of As or Se at the plant, nor have they necessarily demonstrated an added benefit of retention of As and Se under the tested leaching conditions.

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Figure 1. Phase II Total Hg Release

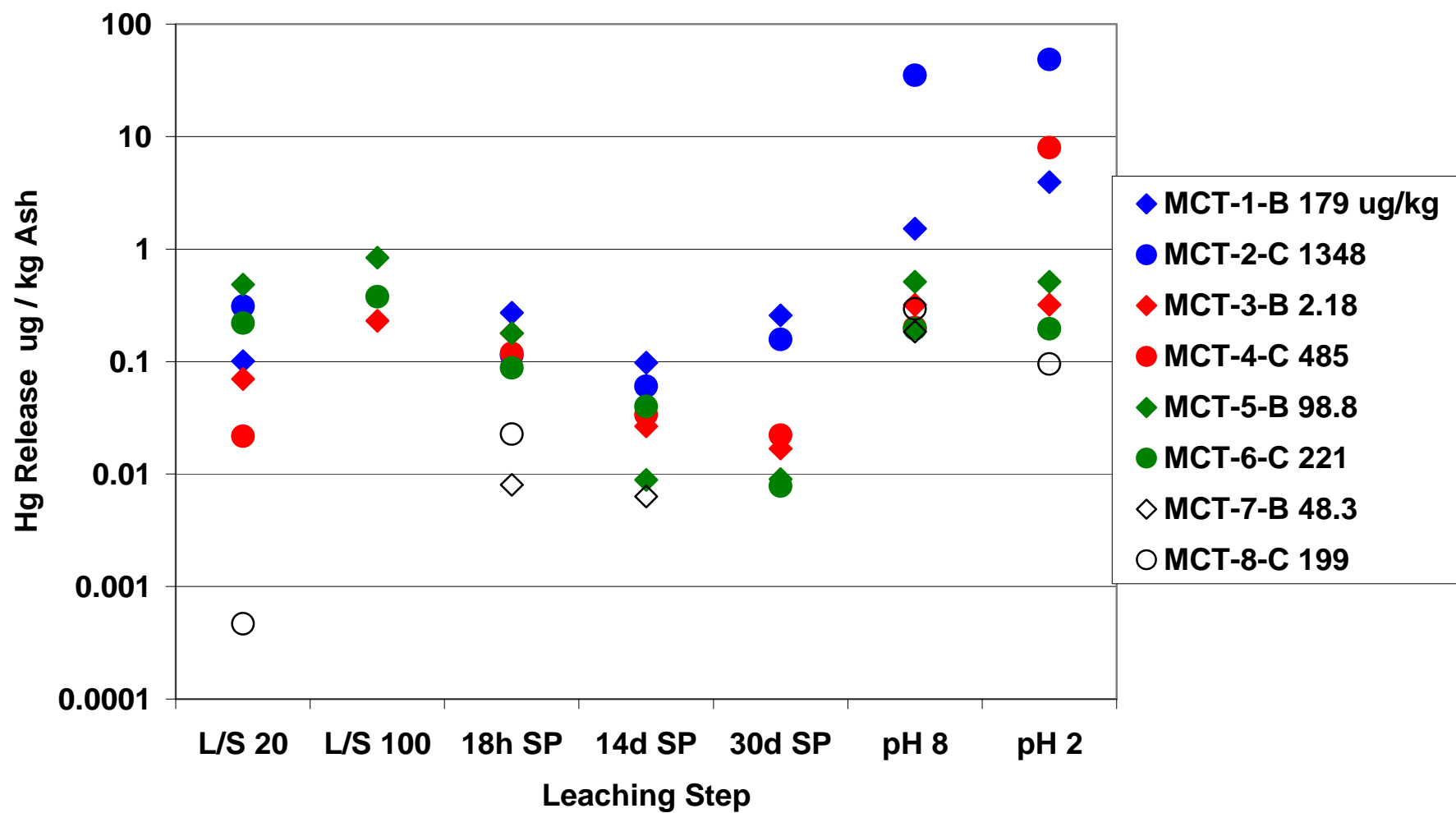


Figure 2. Phase II Leachate Hg Concentrations

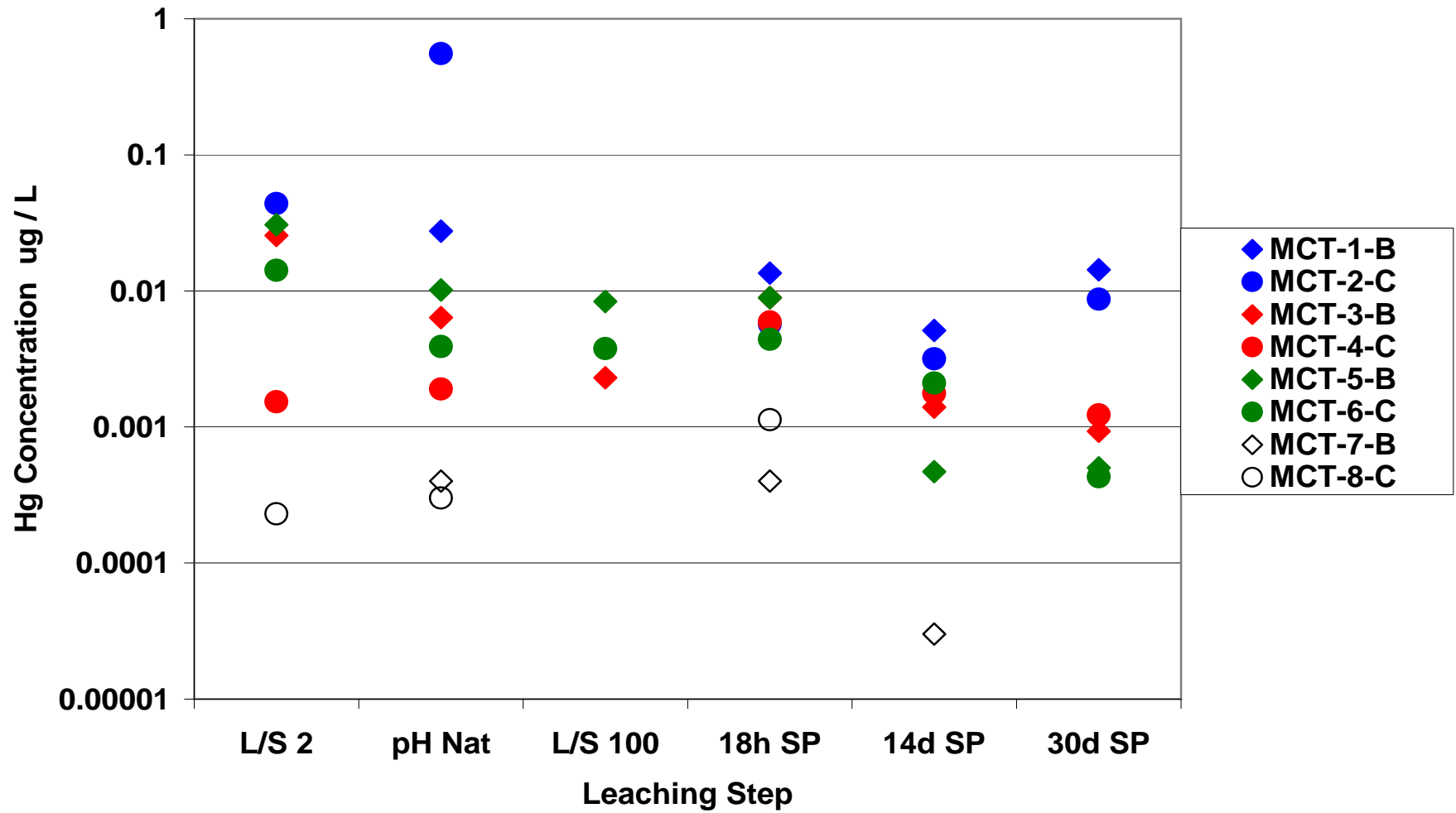


Figure 3. Phase II Hg Release - Time and L/S Ratio

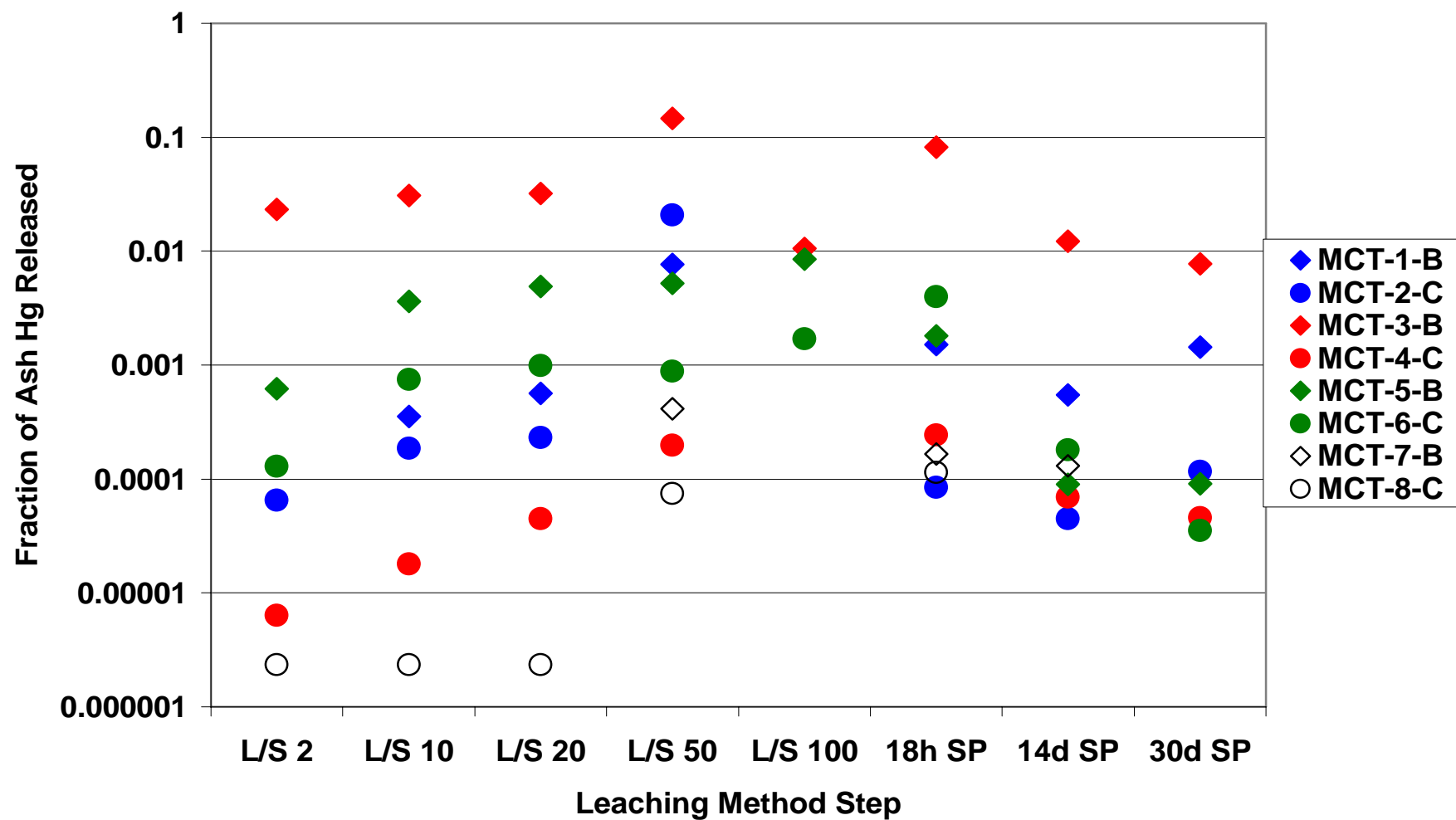


Figure 4. Phase II Hg Release - pH

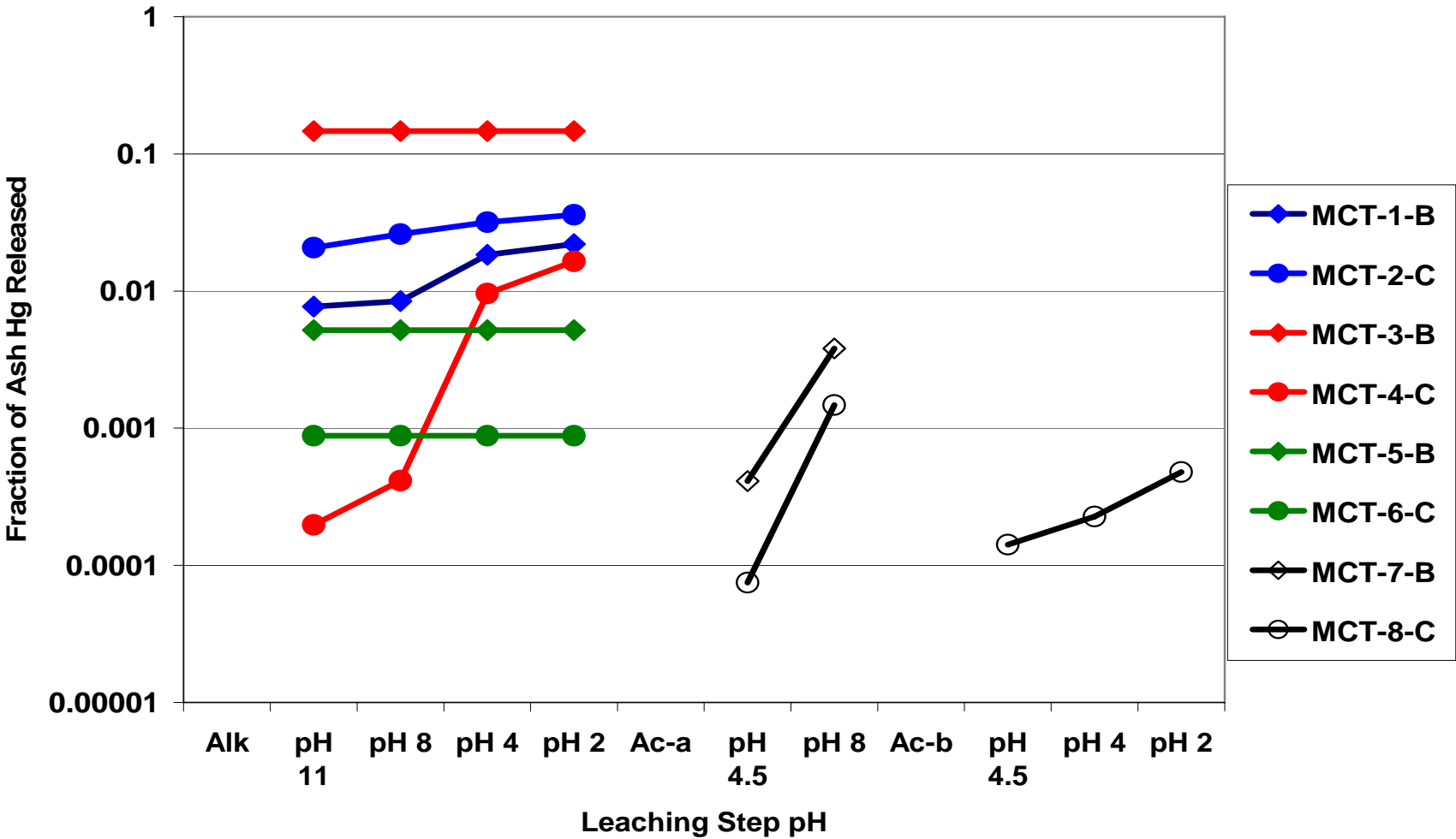


Figure 5. Phase II Mercury Release
1-B 179ug/kg 2-C 1348ug/kg

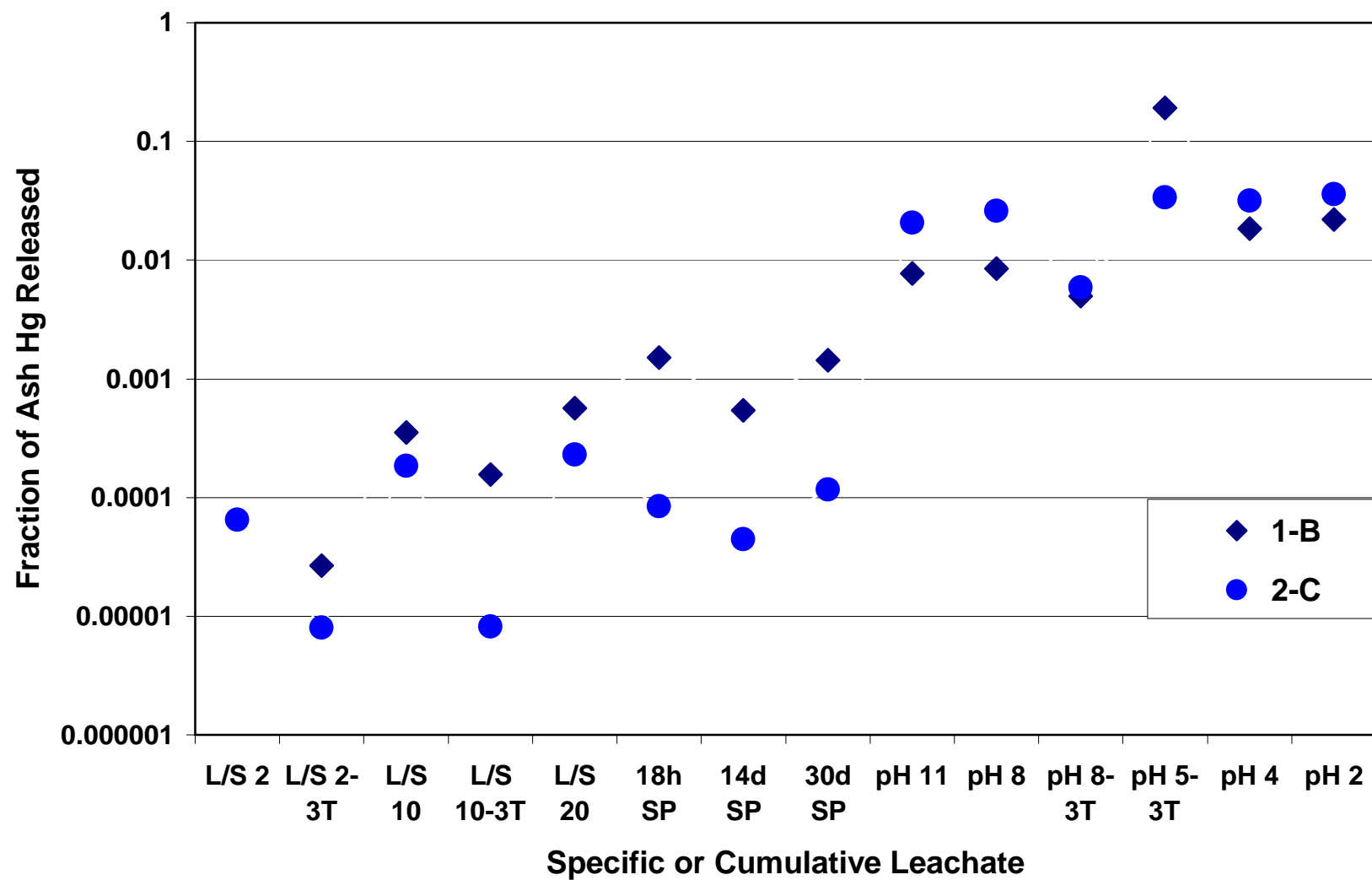


Figure 6. Phase II As Release - pH

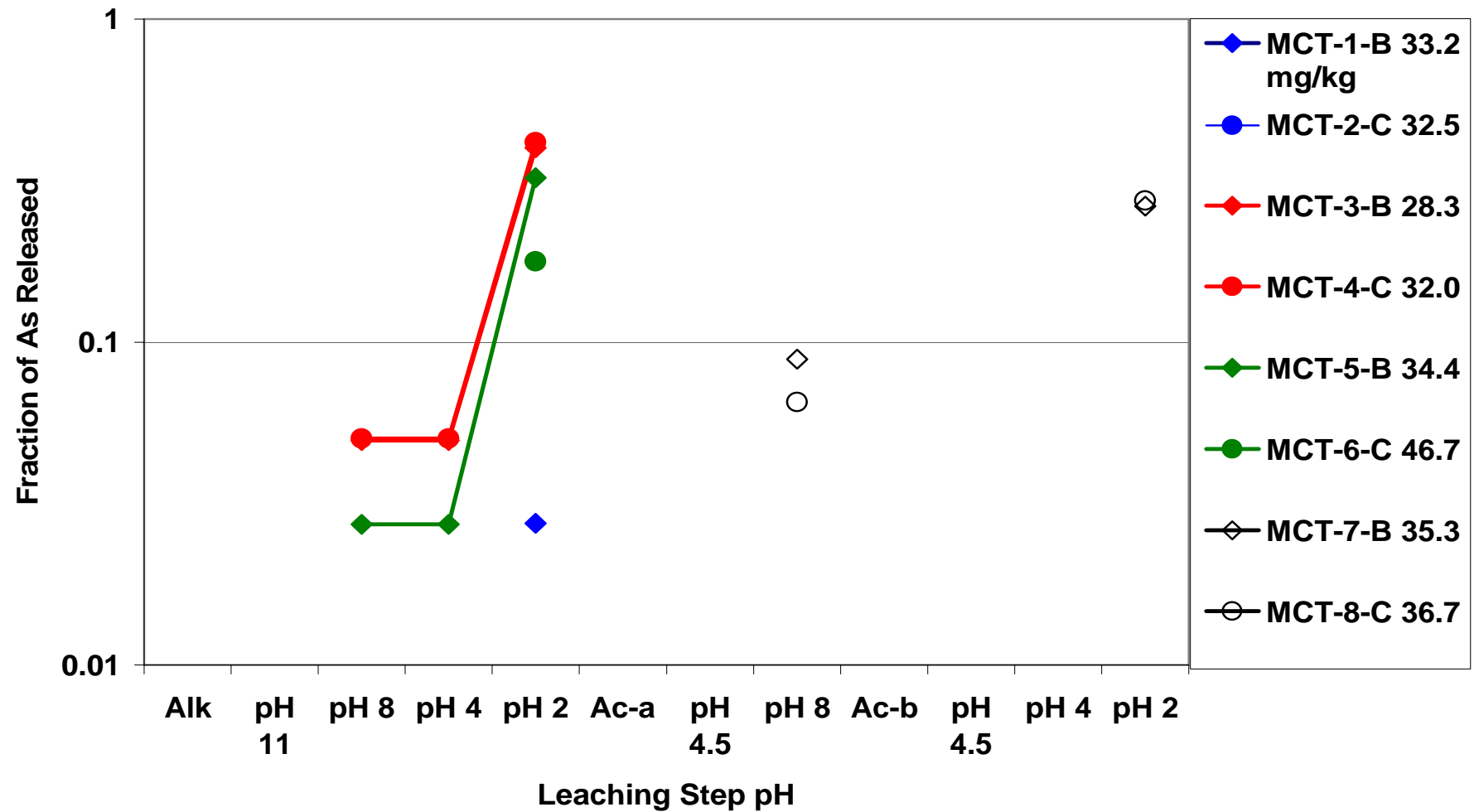


Figure 7. Phase II Arsenic Release
1-B 33,200ug/kg 2-C 33,500ug/kg

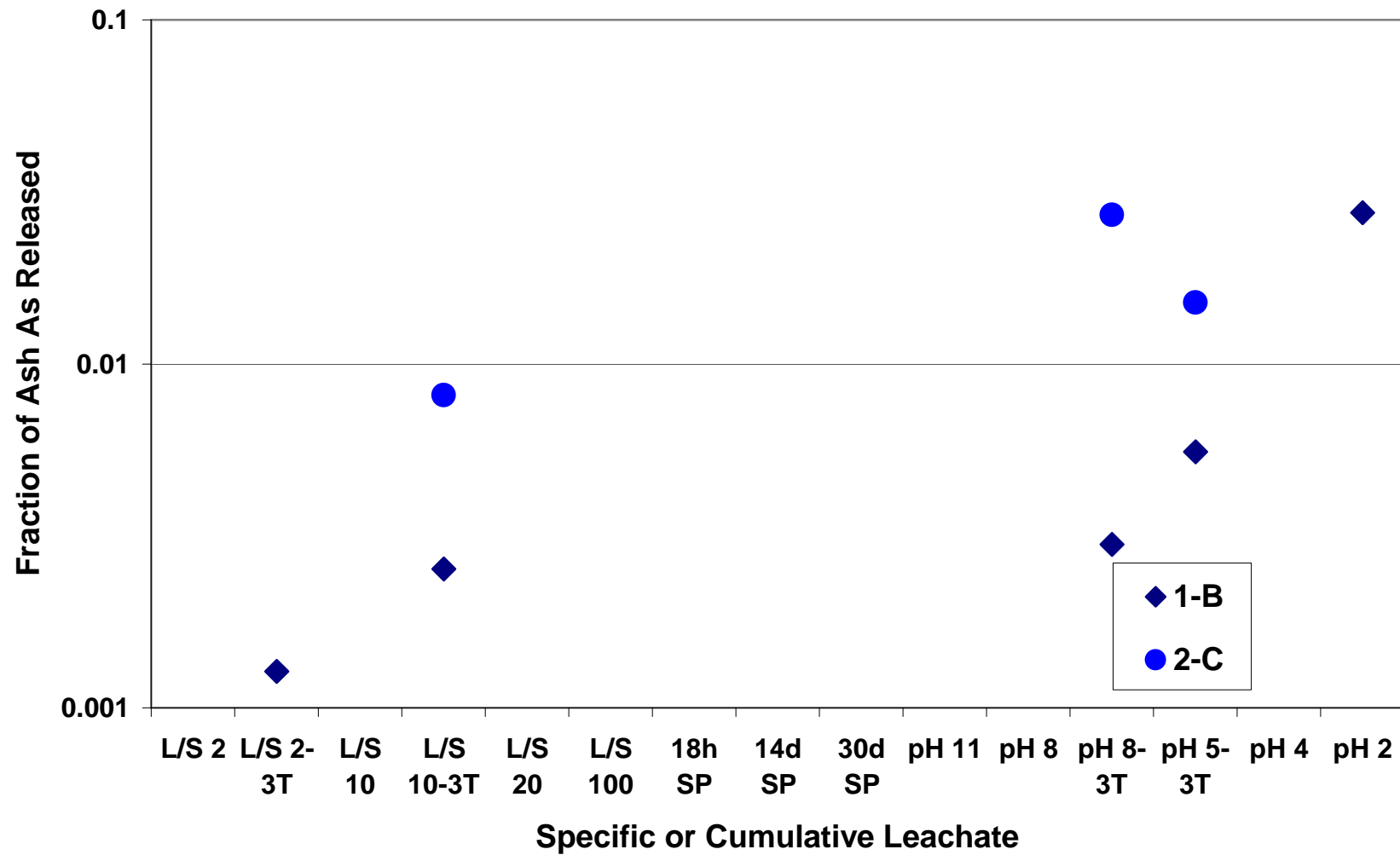


Figure 8. Phase II Total Se Release

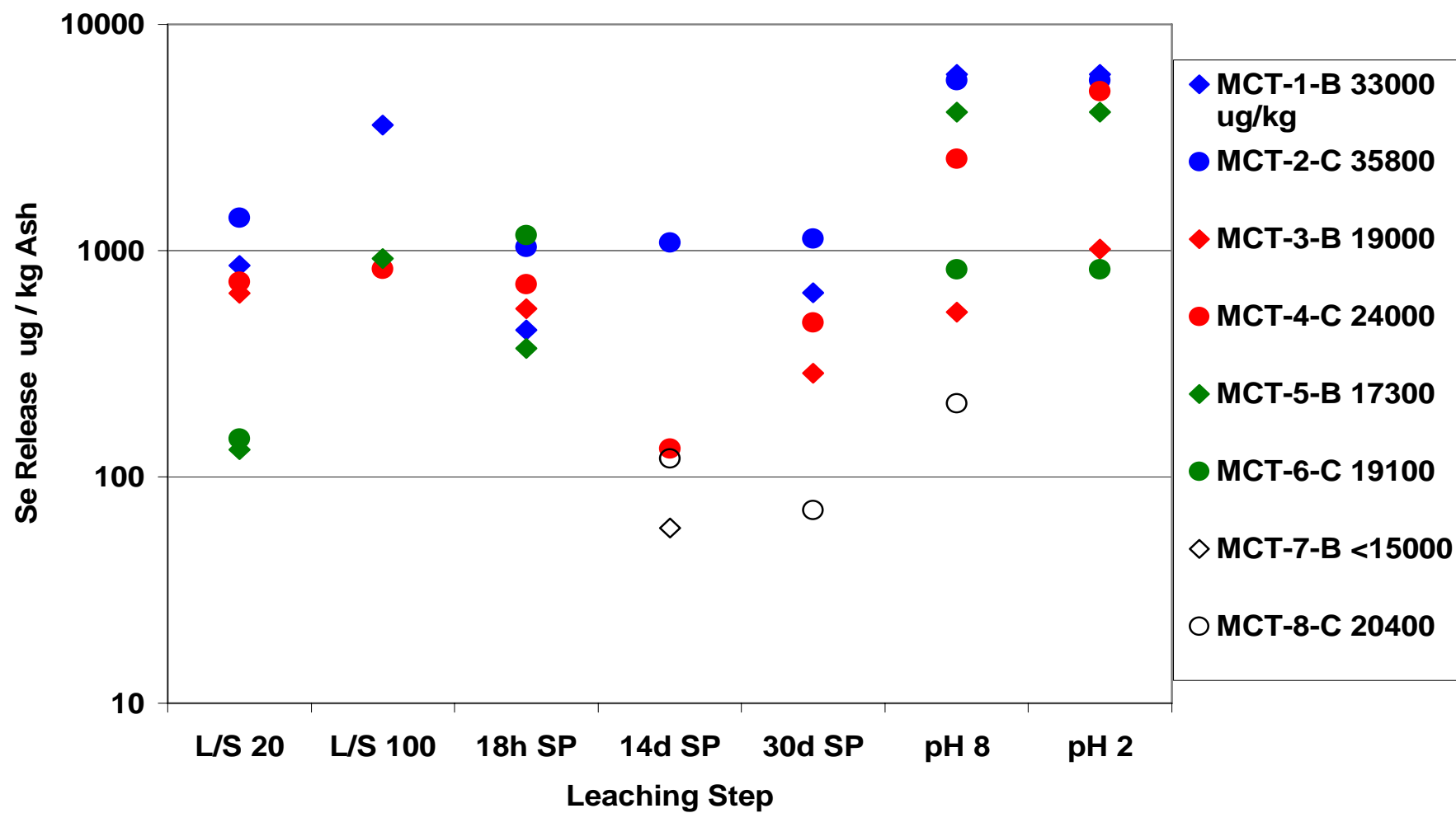


Figure 9. Phase II Leachate Se Concentrations

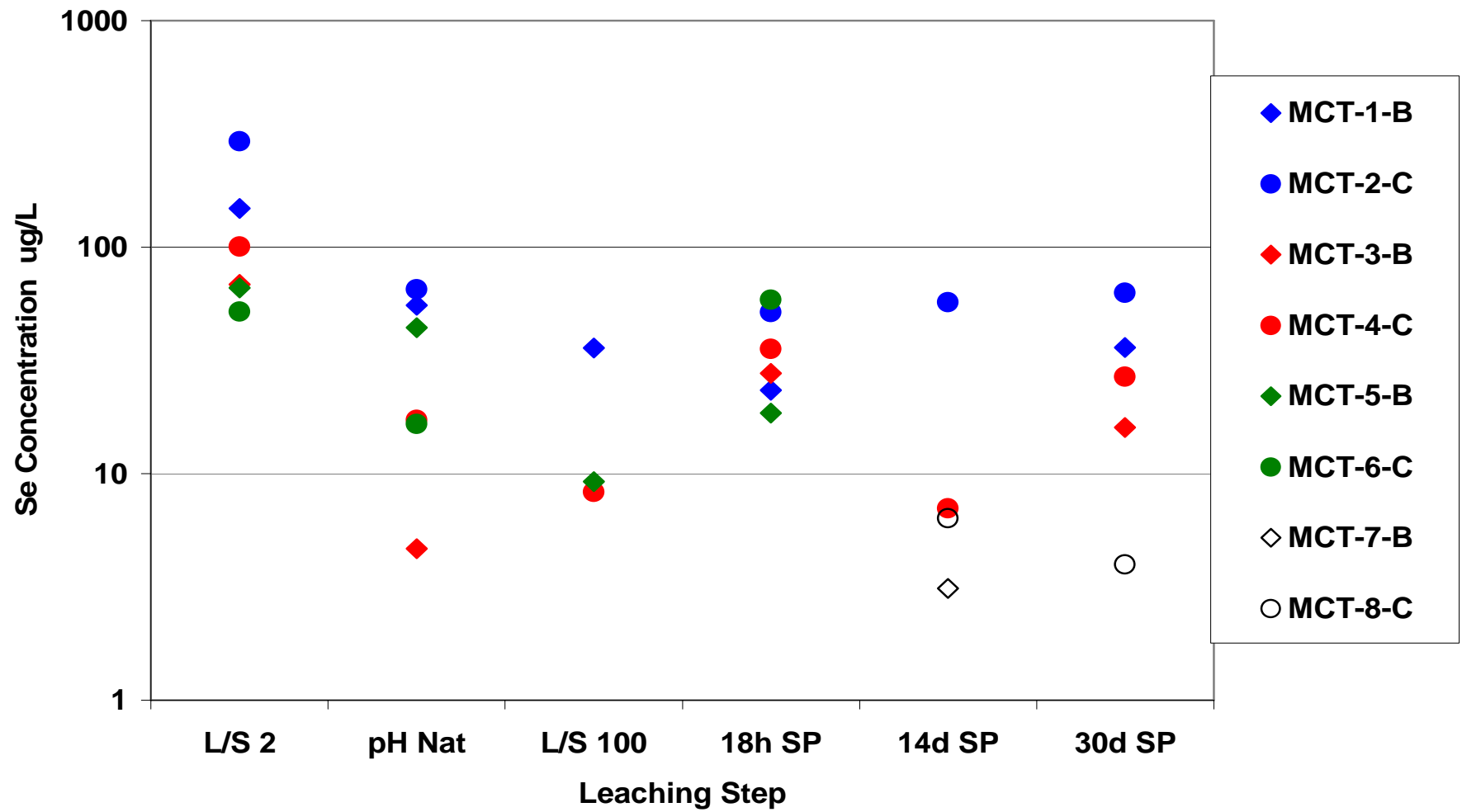


Figure 10. Phase II Se Release - Time and L/S Ratio

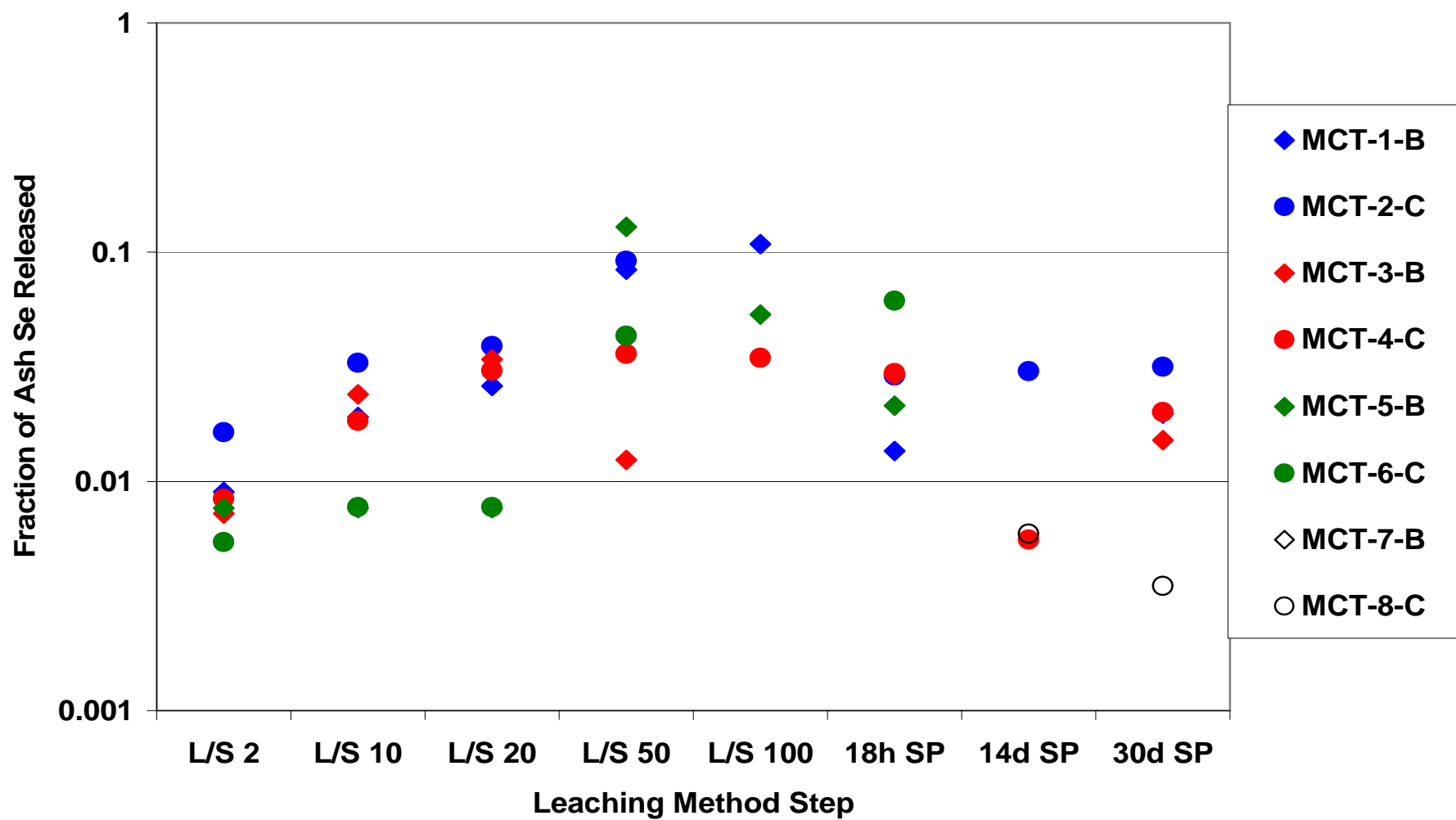


Figure 11. Phase II Se Release - pH

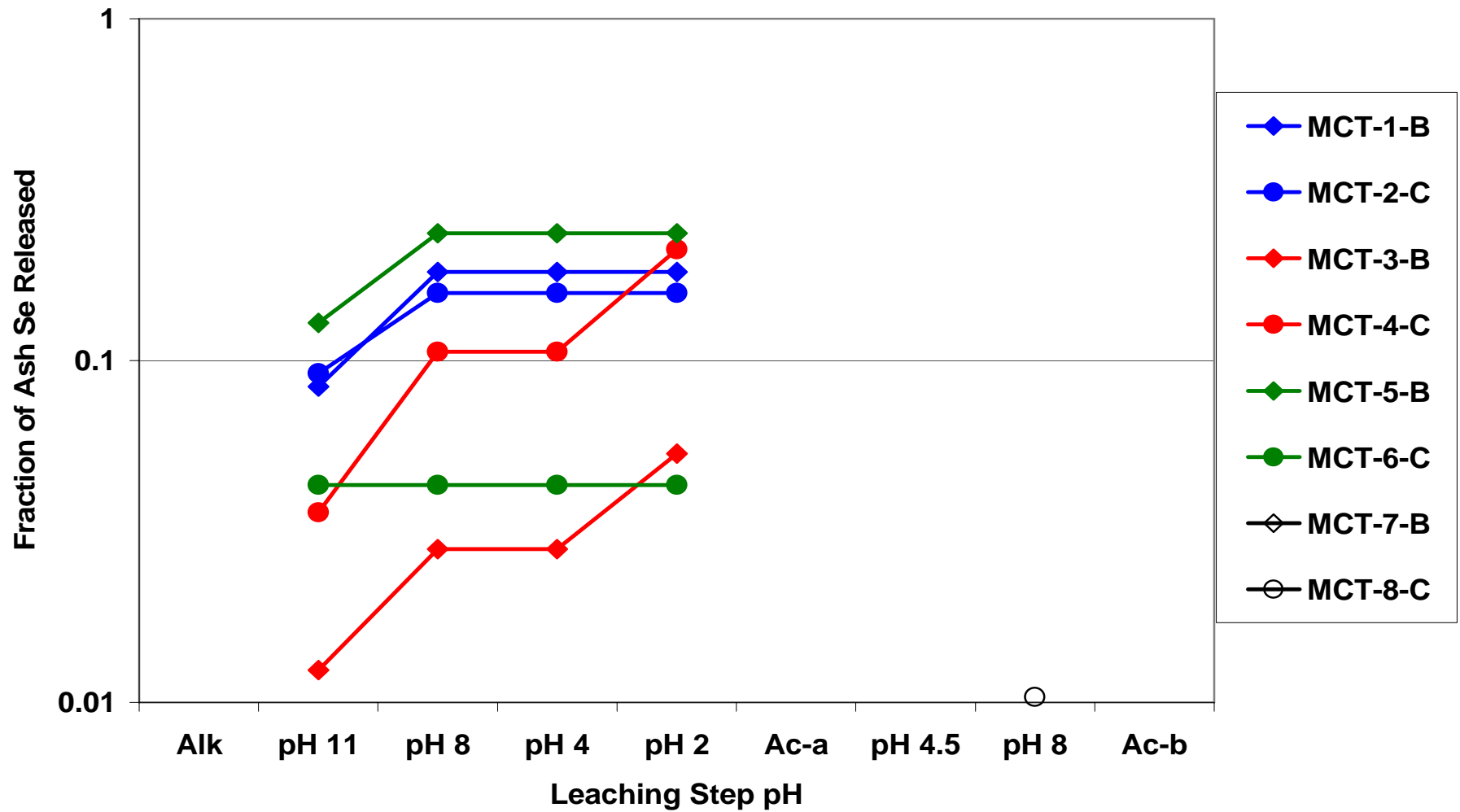
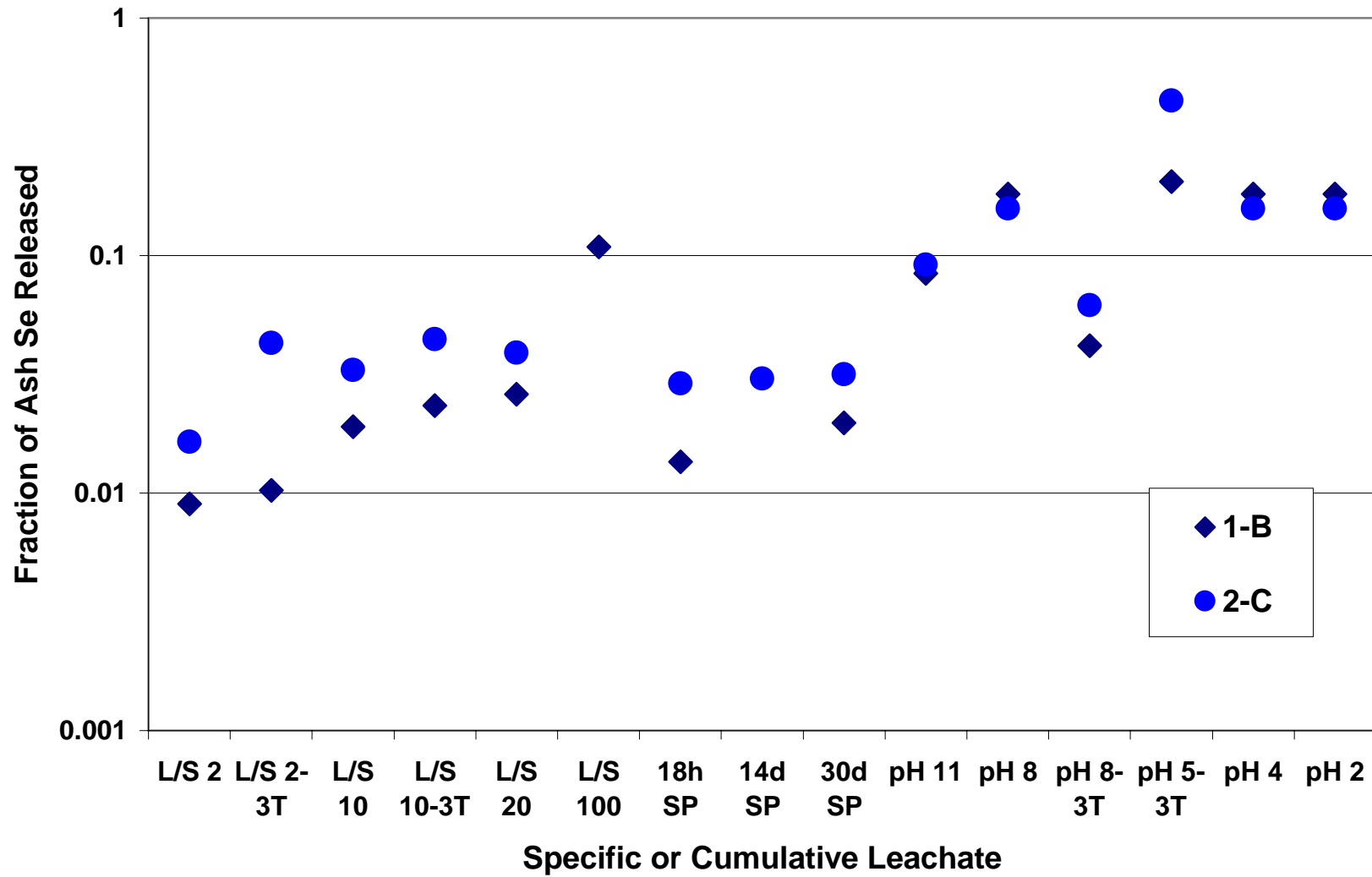


Figure 12. Phase II Selenium Release
1-B 33,000ug/kg 2-C 35,800ug/kg



World of Coal Ash

May 7-10, 2007 Covington, Kentucky



*Leaching of Phase II Mercury
Control Technology By-
products.*

*Peter A. Hesbach
Edward K. Kachur*

Peter A. Hesbach, Research Chemist, Environmental Science Division
National Energy Technology Laboratory



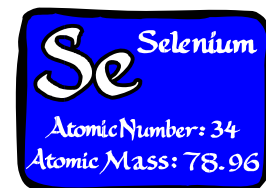
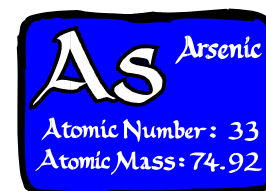
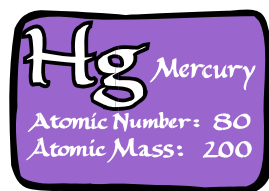
Background

- **US EPA issued final rulings for Hg control.**
- **Clean Air Interstate Rule – Hg capture side benefit.**
- **Clean Air Mercury Rule – Focused Hg reduction.**
- **Anticipated by: DOE / Fossil Energy / NETL / Innovations for Existing Plants Program.**
- **EPRI, US EPA, State and Local Governments, Research Organizations and Universities.**
- **IEP RD&D Program evaluating performance and cost of mercury control.**



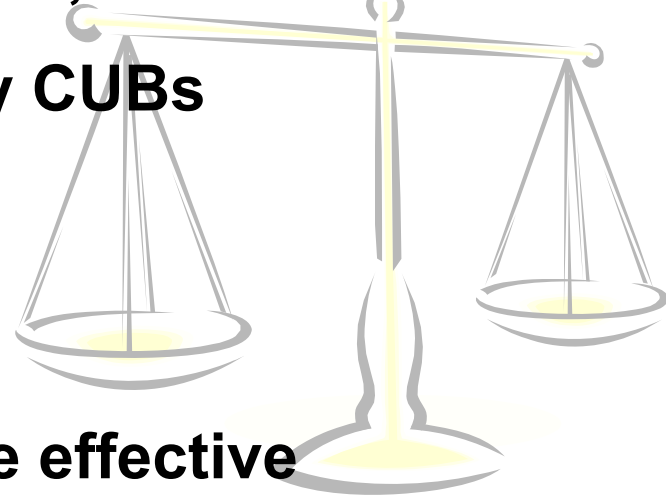
Technical Issues

- Flue gas Hg captured in condensed phases.
- Altered solid by-products and FGD material.
- Concern of potential environmental release.
- Economics - lost sales and disposal costs.
- Challenge to expanded use of coal utilization by-products (CUB).



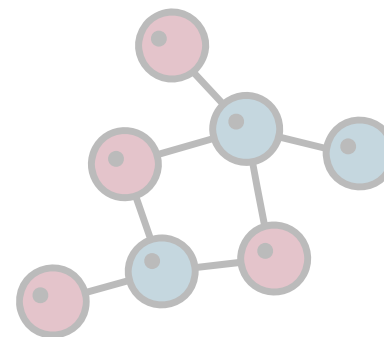
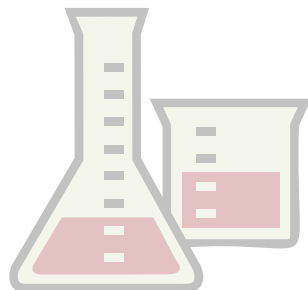
Project in Perspective

- **Mercury Control Phase II – Development and Testing and of Novel Concepts.**
- **Matrix of particulate control, coals, locations.**
- **Baseline and control technology CUBs collected from coal-fired plants.**
- **Constituent release evaluated.**
- **Potential trade-off between more effective capture and more permanent sequestration.**

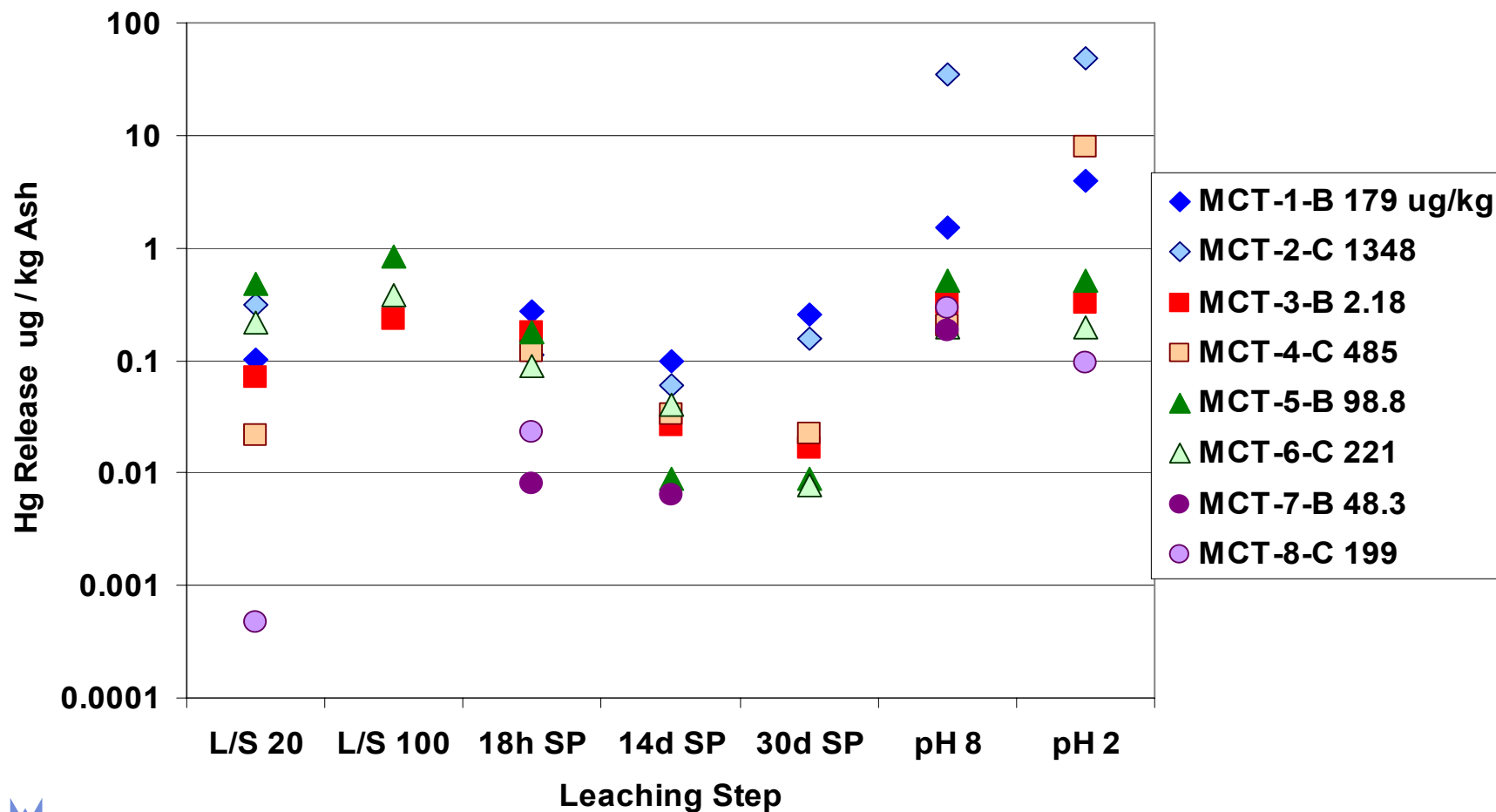


Technical Approach – Aqueous Leaching

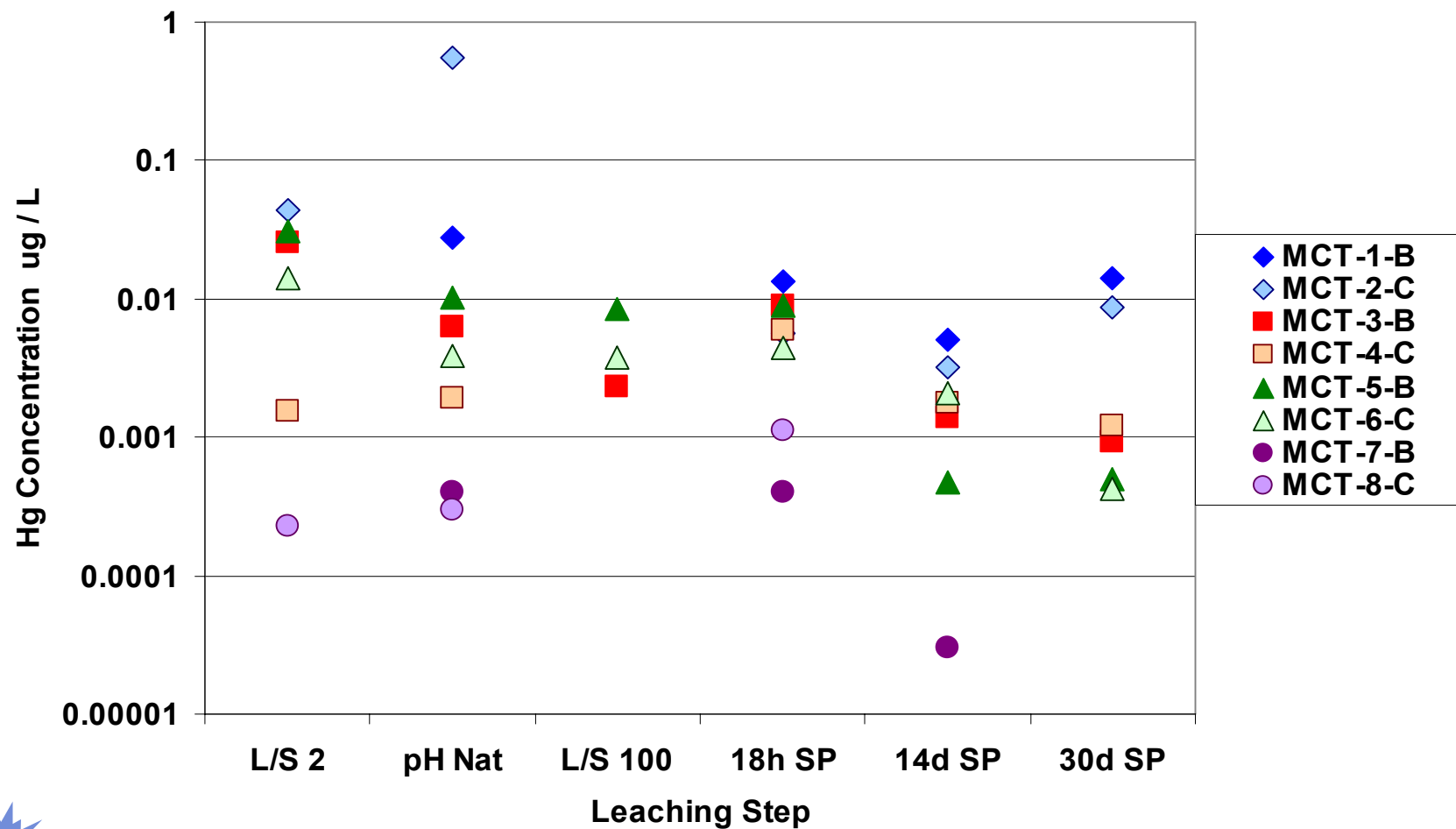
- **NETL Serial Batch Leaching Procedure**
Availability – L/S=50, stirred 2-4 hrs/step
pH sequence – natural \rightarrow 8 \rightarrow 4 \rightarrow 2 [\rightarrow 1.4]
natural \rightarrow 4 \rightarrow 2 [\rightarrow 1.4] and natural \rightarrow 8
L/S sequence 2 \rightarrow 8 \rightarrow 10 plus L/S=100
- **Synthetic Precipitation – L/S=20, Eastern solution**
18 hrs, 14 days, 30 days.
- **Integrated Framework Evaluation – 24 hrs**
Target integer pH 12-3 [<2], L/S=10
L/S series – 10, 5, 2, 1 (1/2).



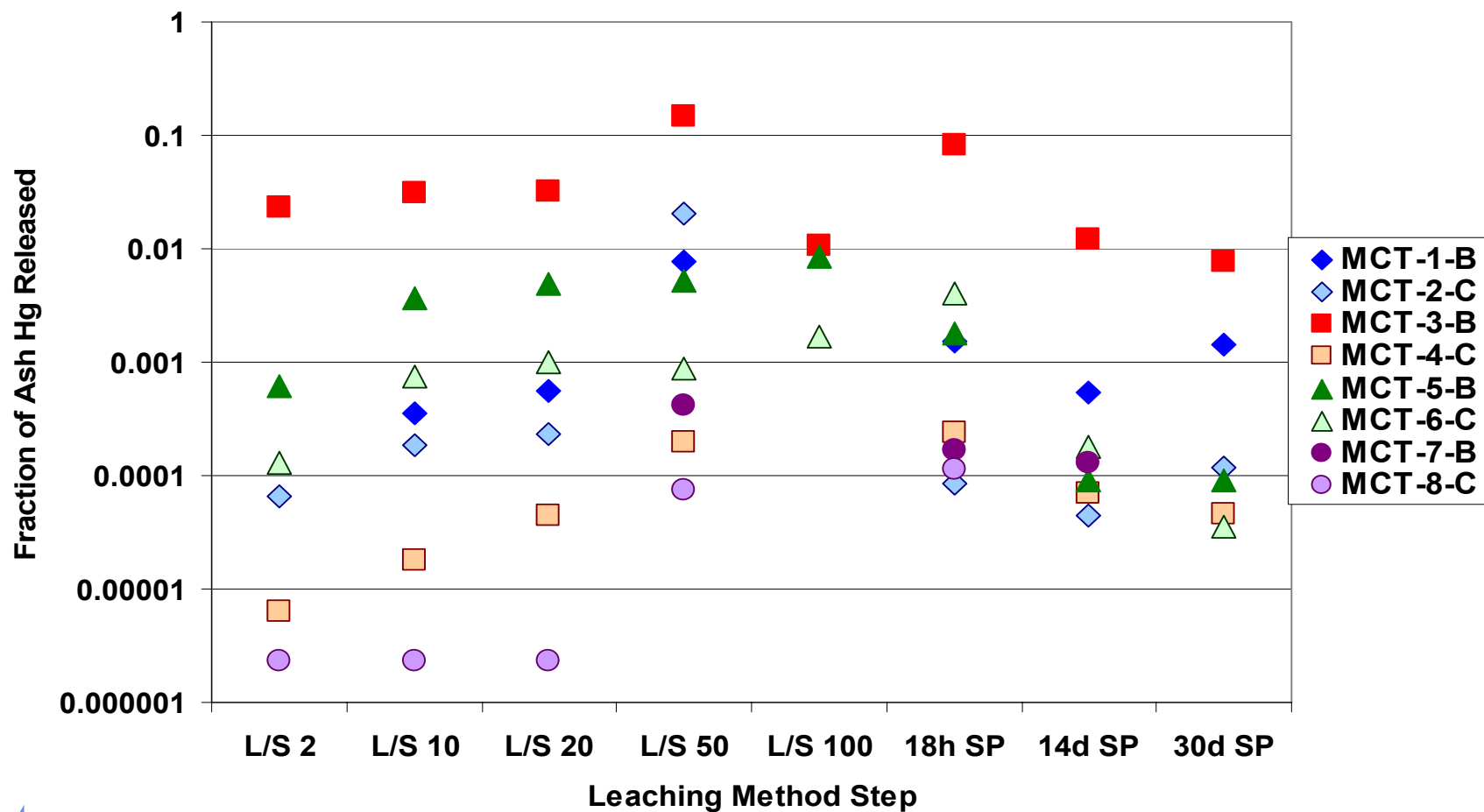
Phase II Total Mercury Release



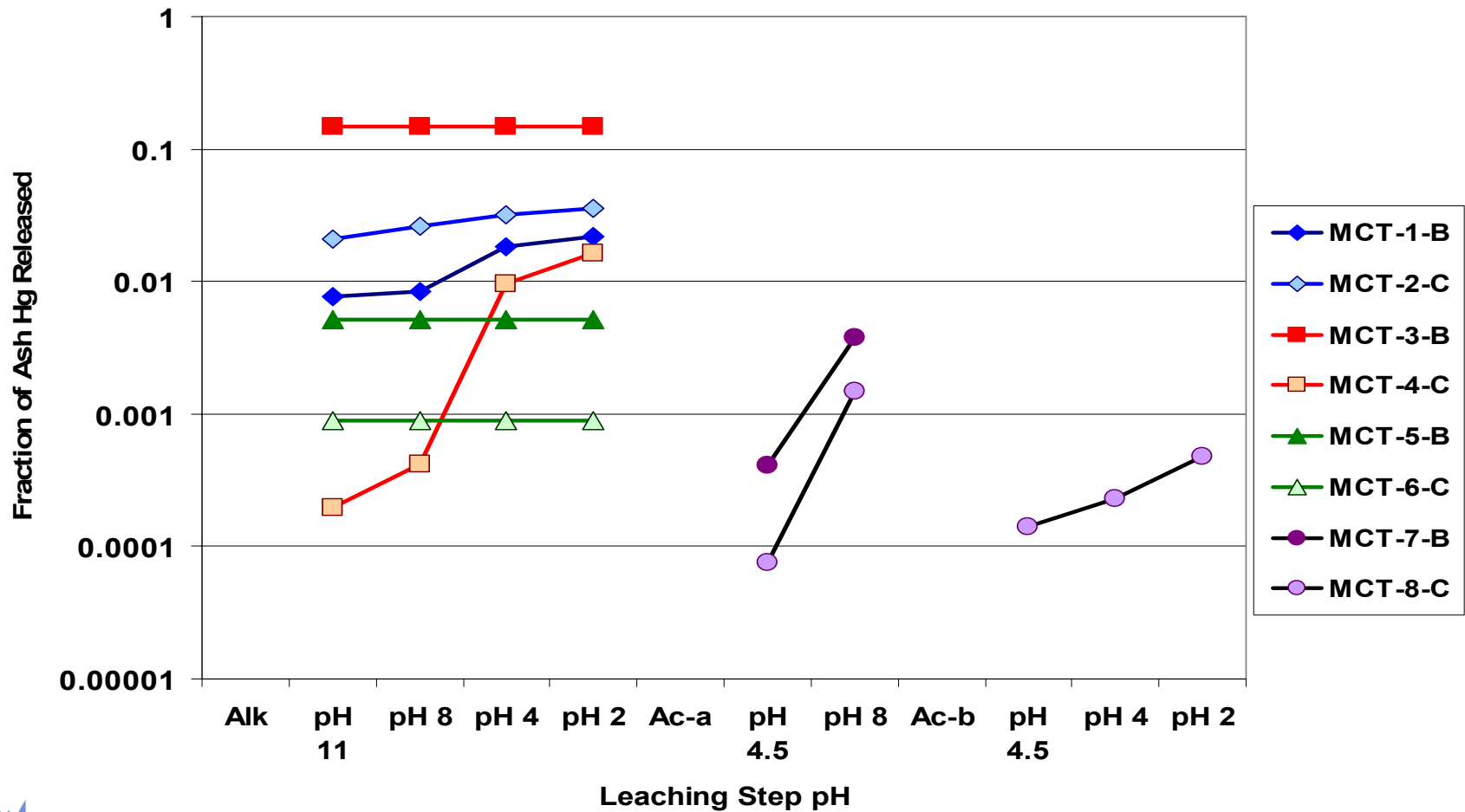
Phase II Leachate Mercury Concentrations



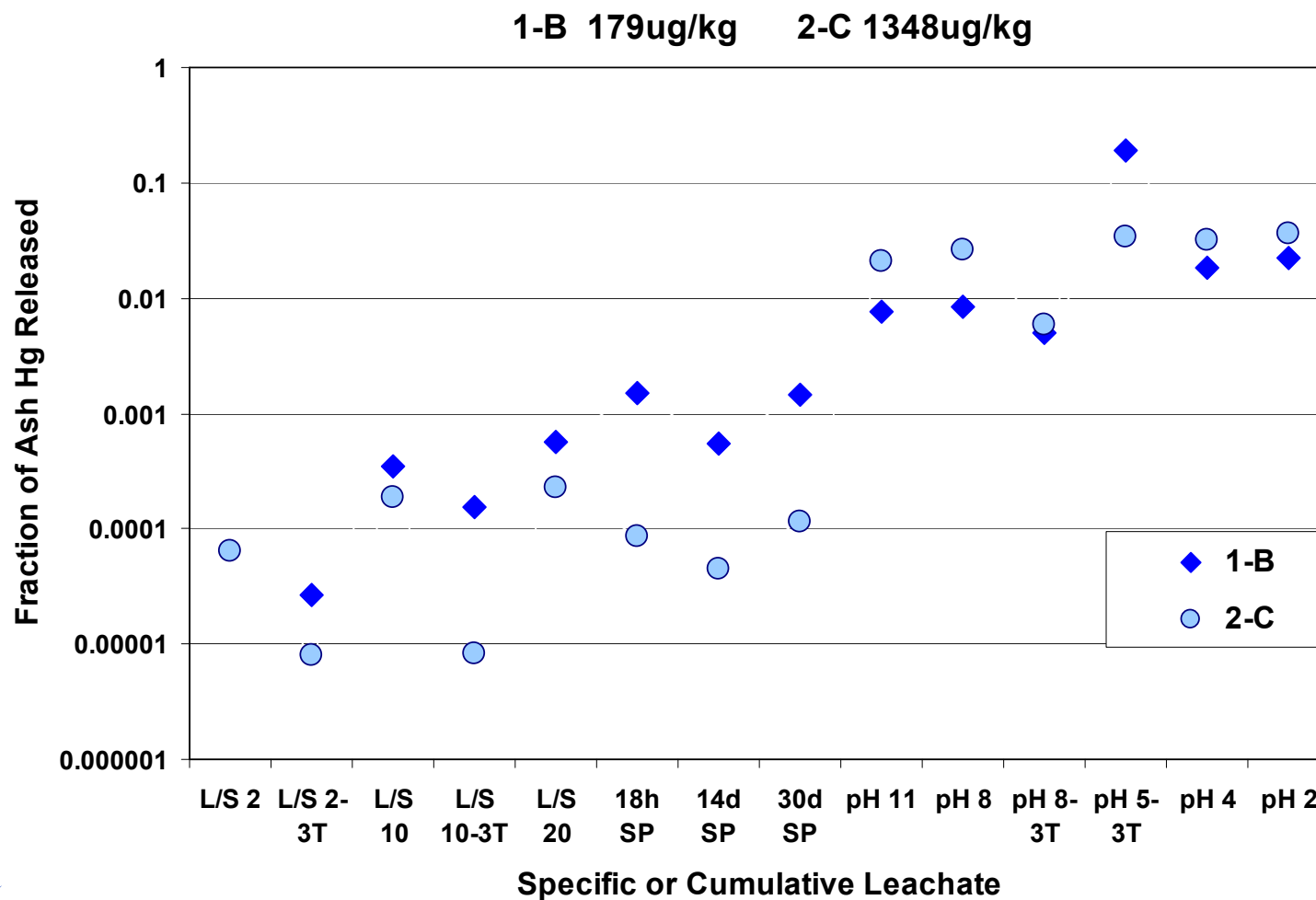
Phase II Hg Release - Time and L/S Ratio



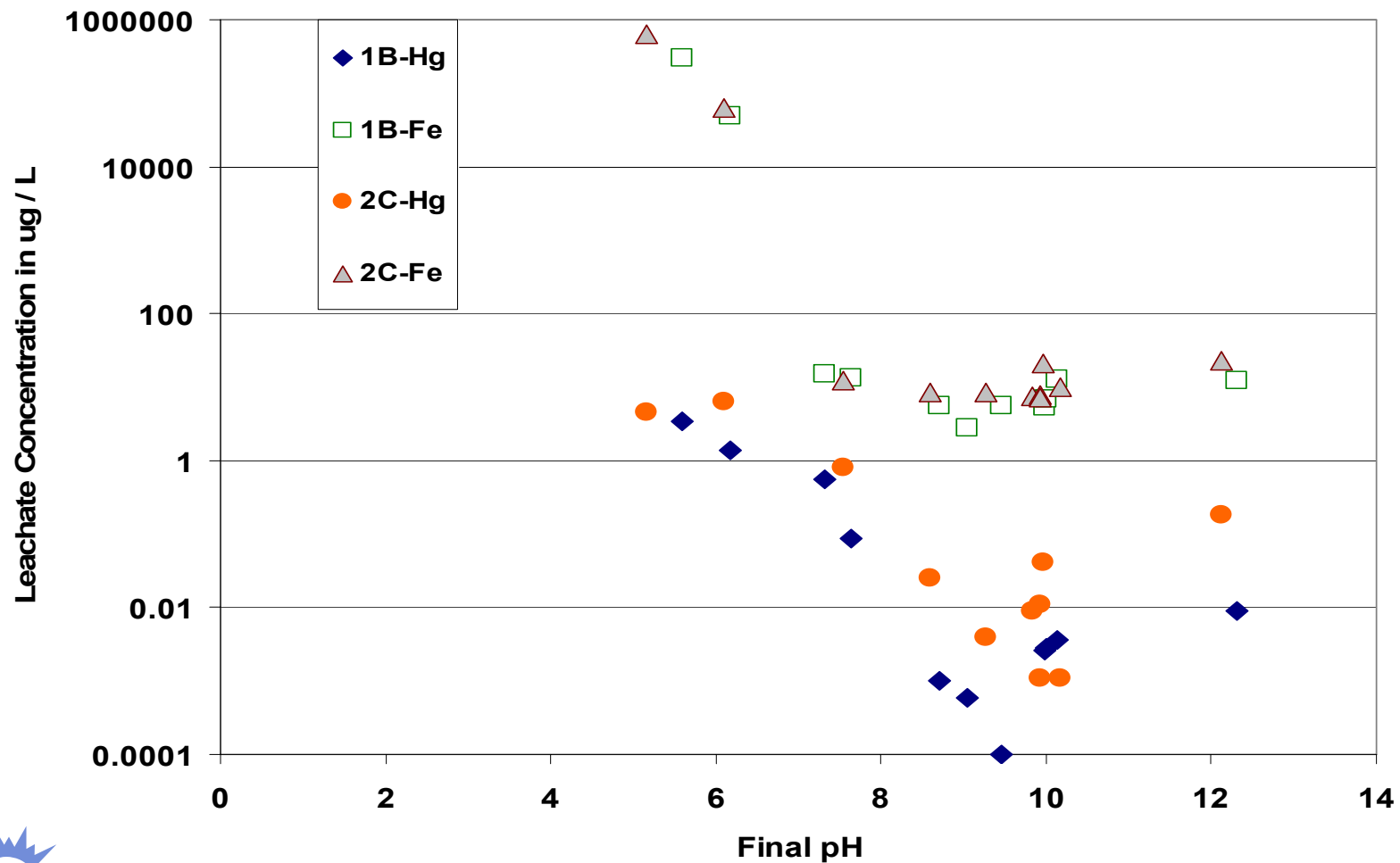
Phase II Mercury Release - pH



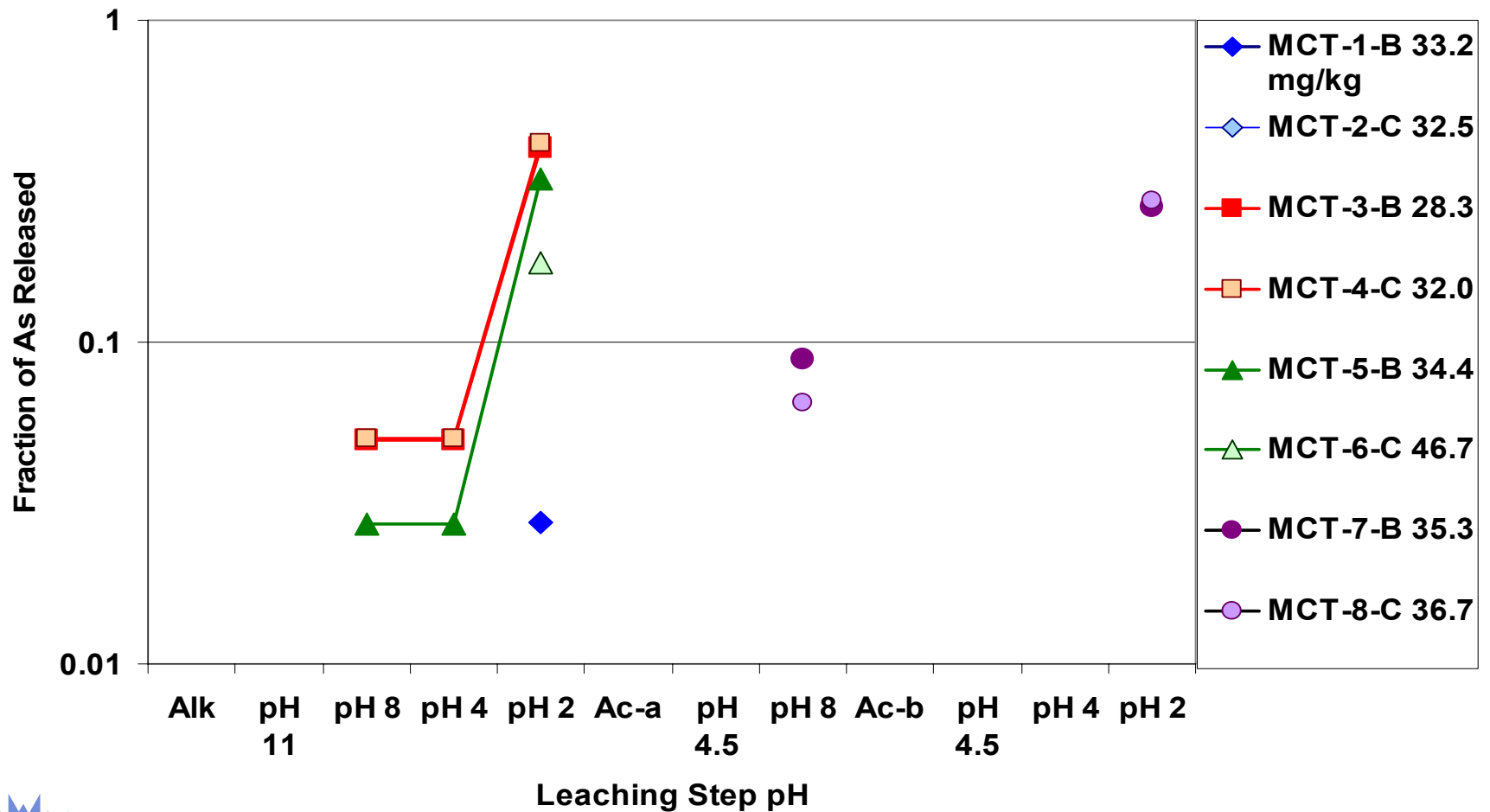
Phase II Mercury Release



Hg and Fe – Concentration by Tier 2B pH

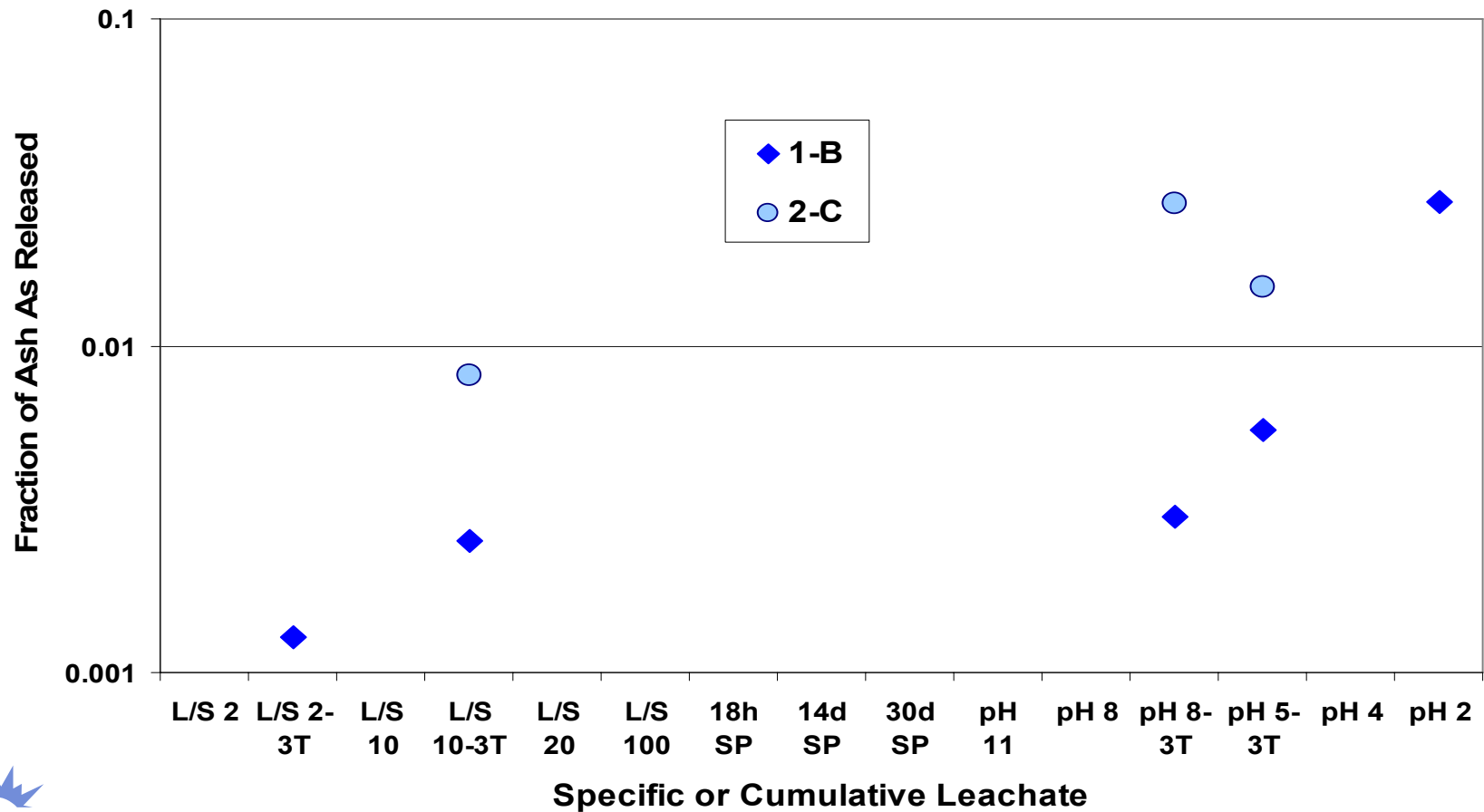


Phase II Arsenic Release - pH

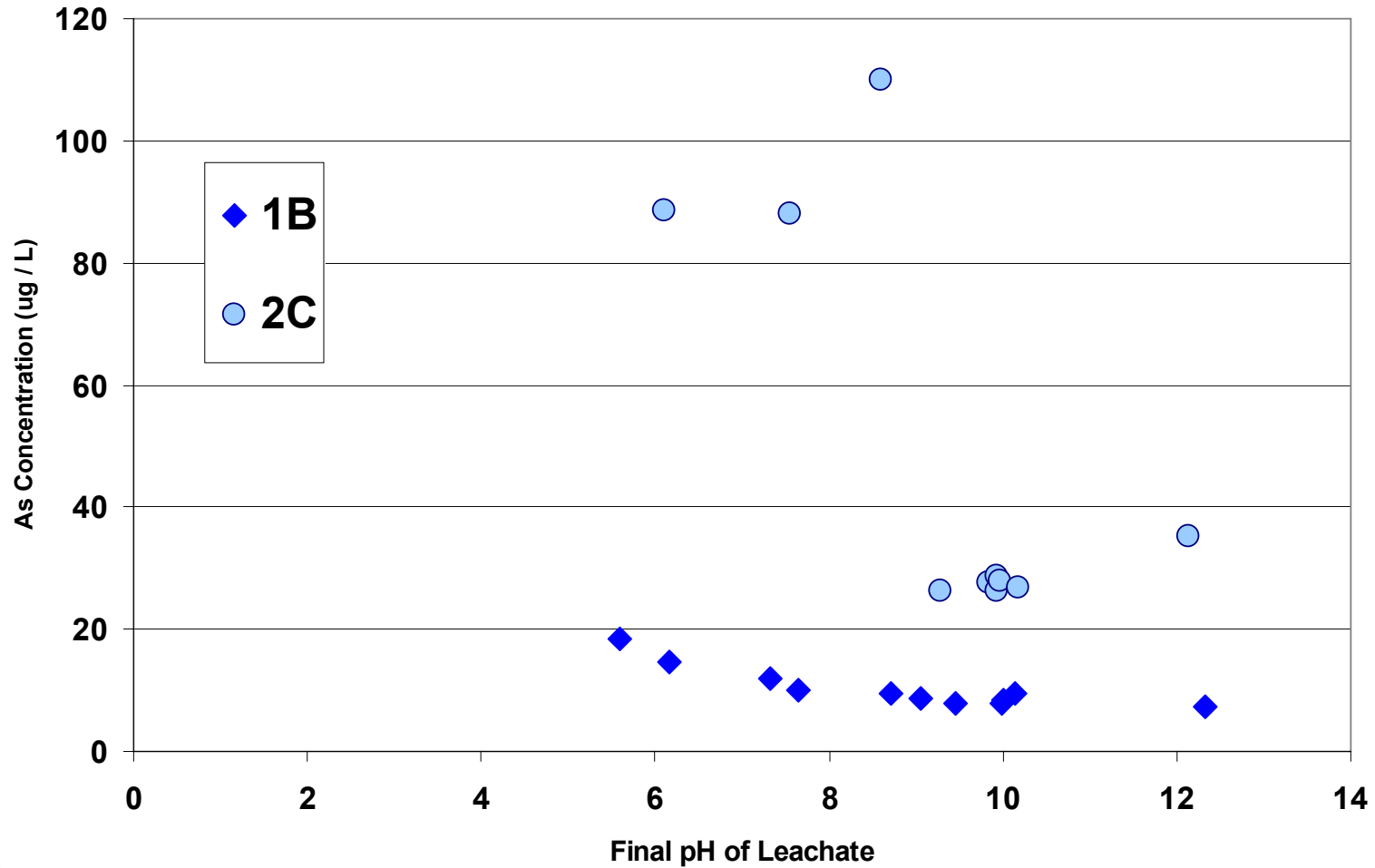


Phase II Arsenic Release

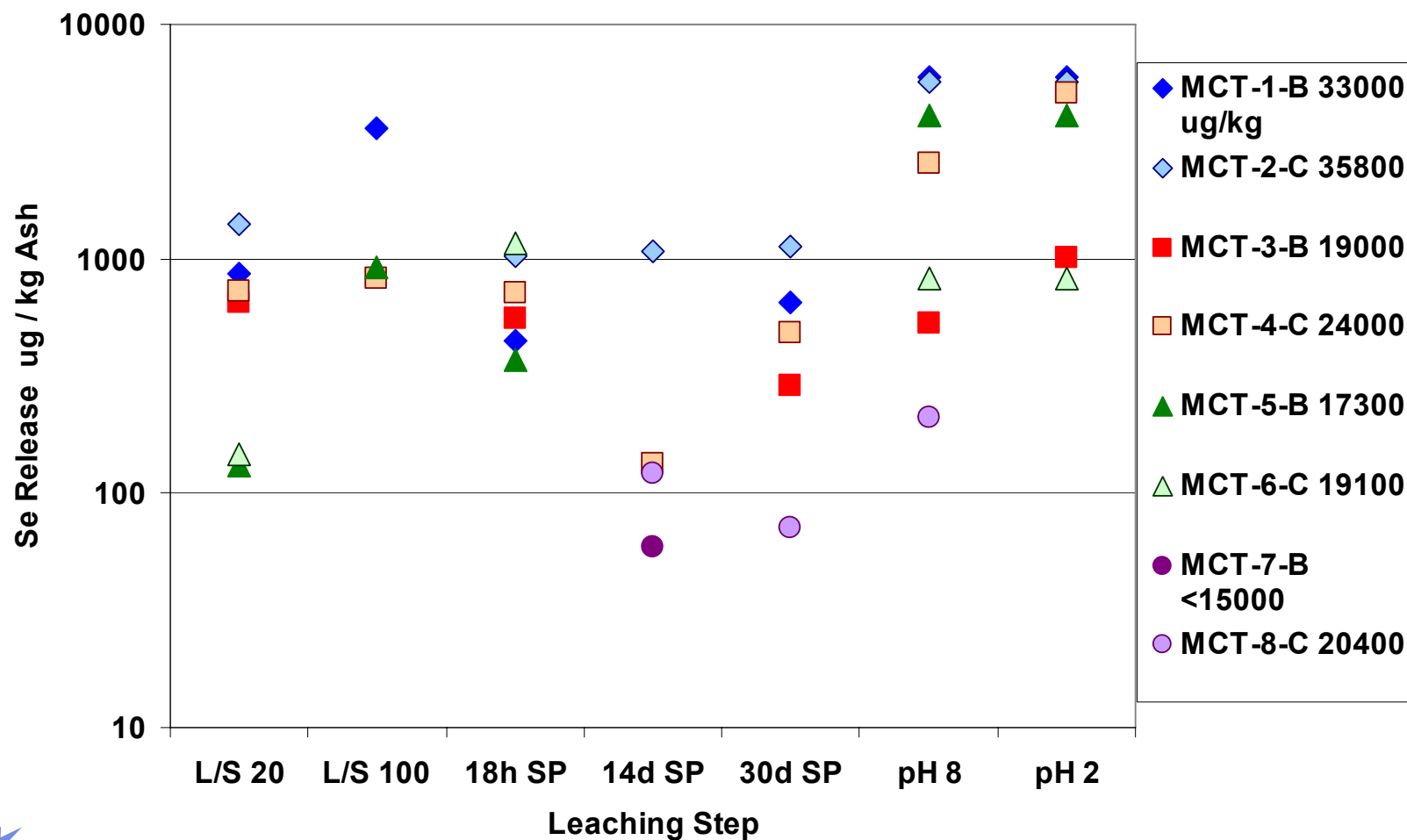
1-B 33,200ug/kg 2-C 33,500ug/kg



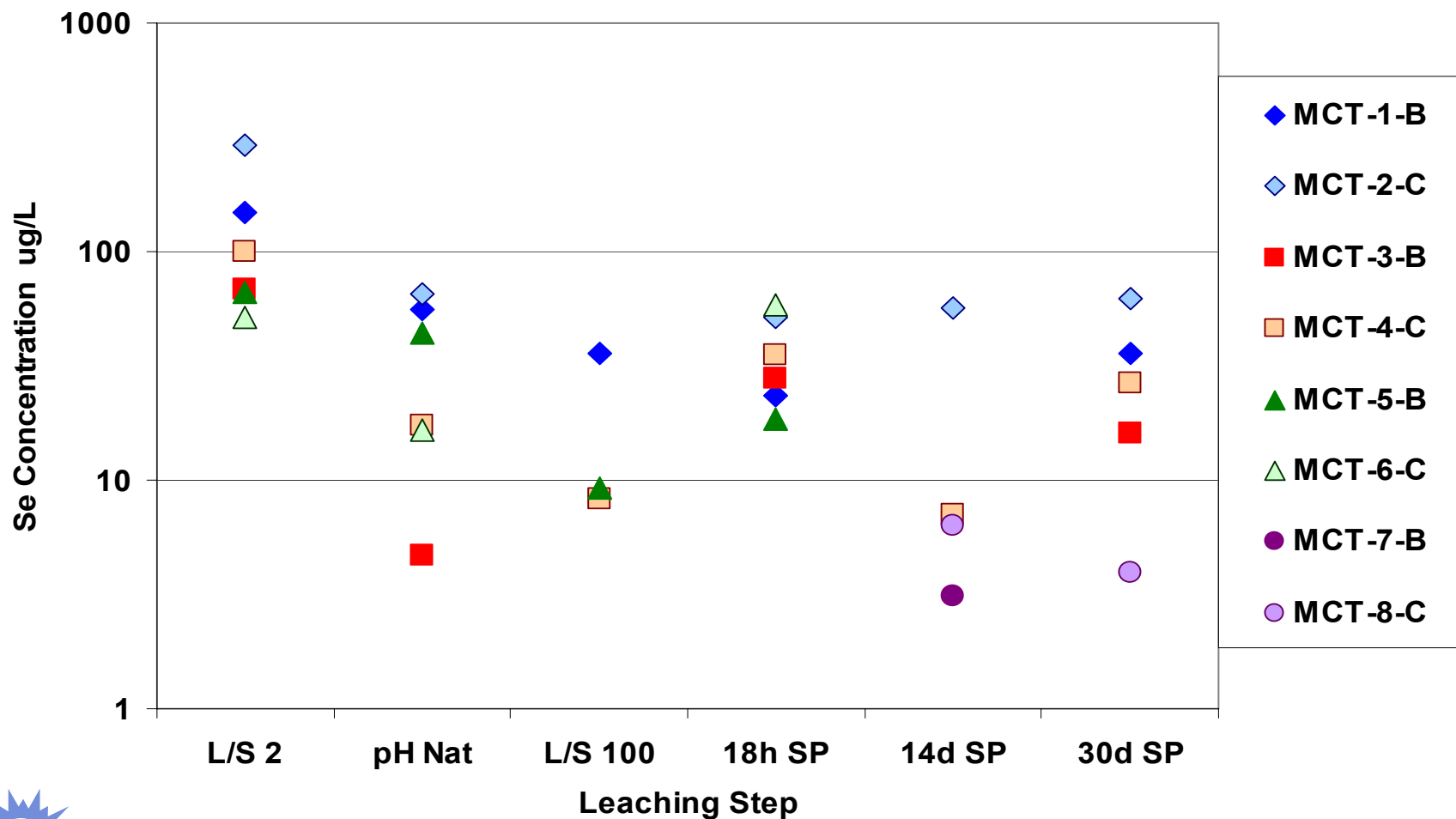
As Release - Concentration by Tier 2B pH



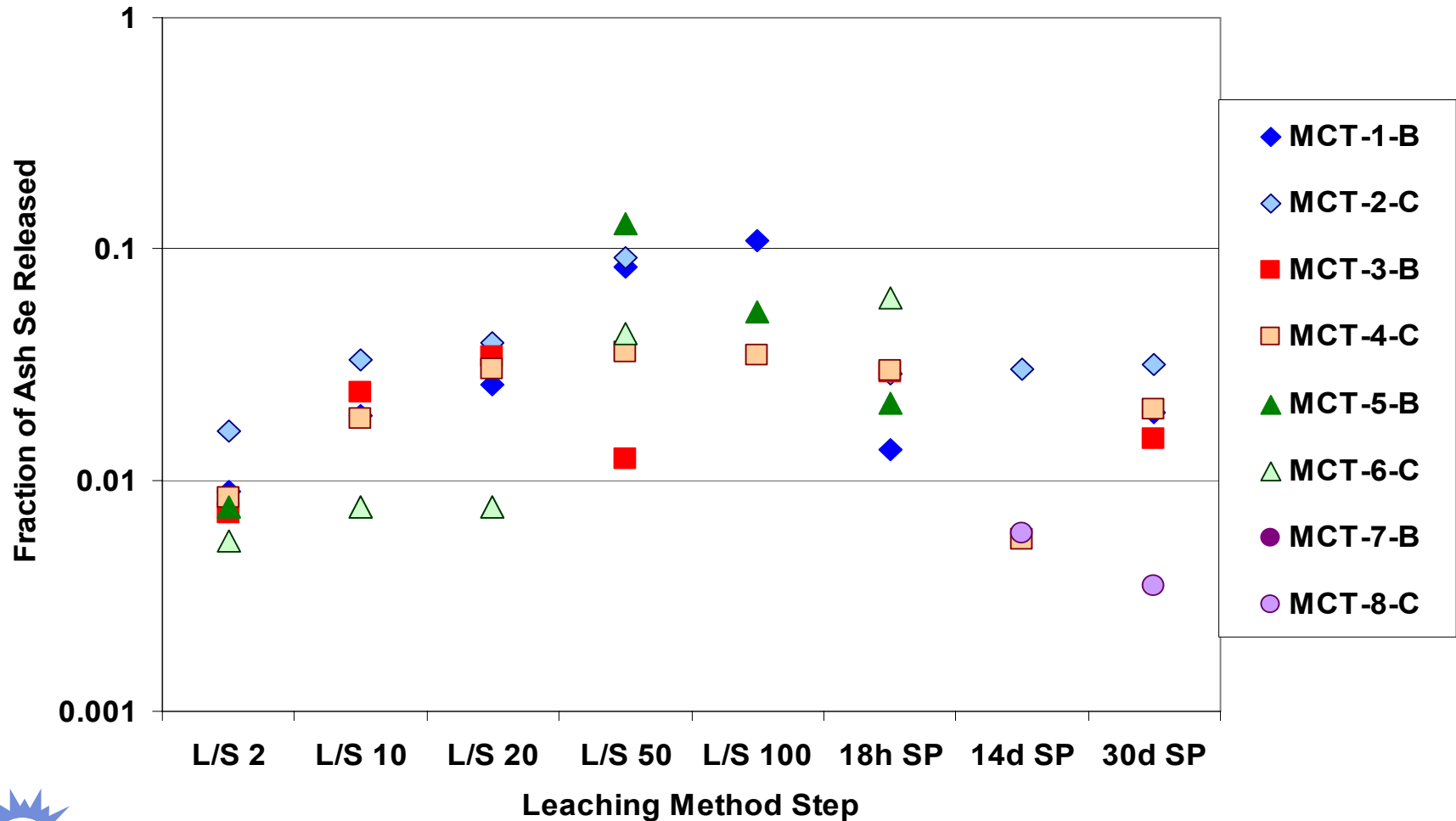
Phase II Total Selenium Release



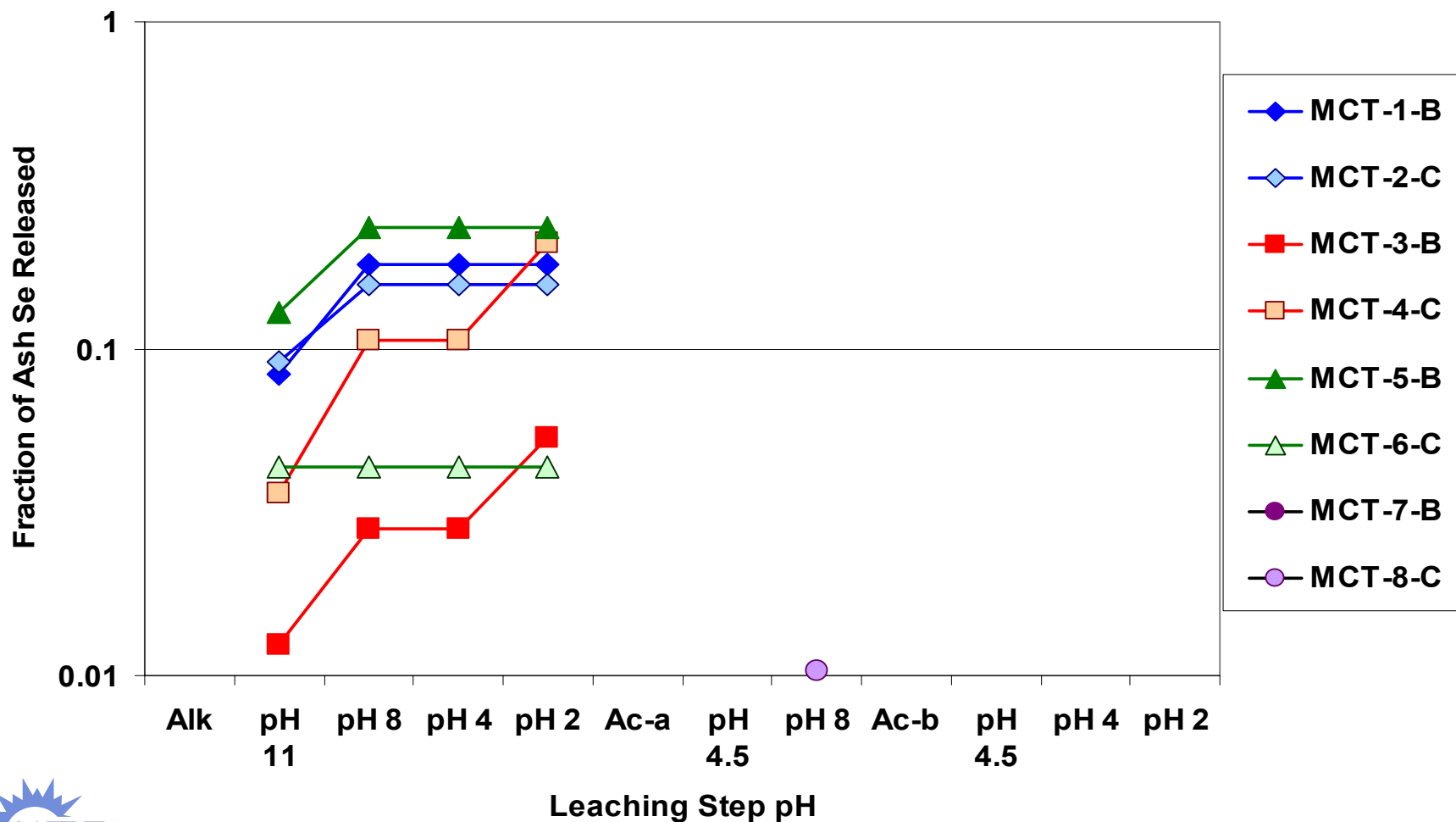
Phase II Leachate Selenium Concentrations



Phase II Se Release - Time and L / S Ratio

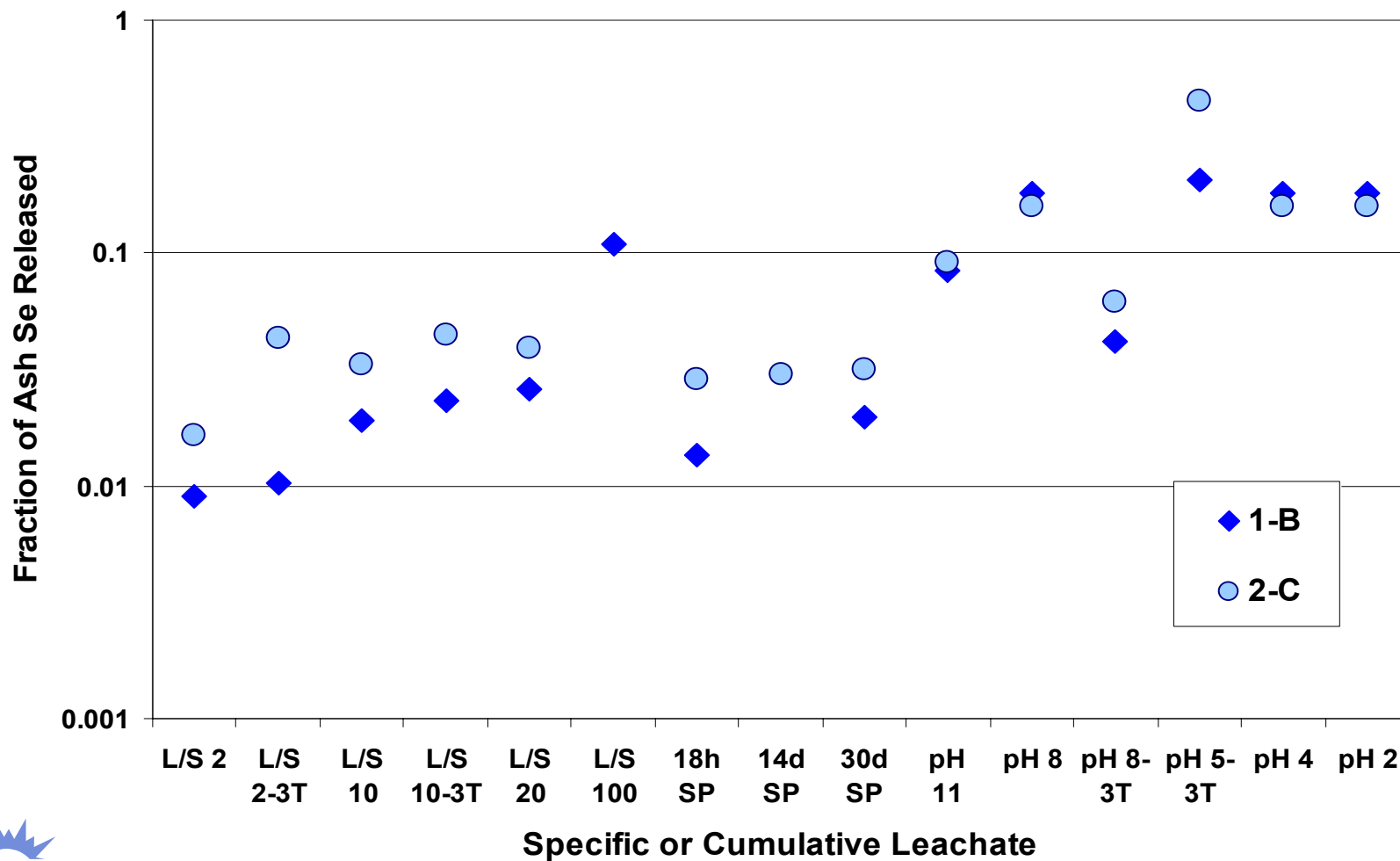


Phase II Selenium Release - pH



Phase II Selenium Release

1-B 33,000ug/kg 2-C 35,800ug/kg



Summary

- Options for Mercury capture from flue gas.
- Effective sequestration of captured Hg.
- Some Hg control technology approaches do not aid capture of As or Se.
- Observed As release under acidic conditions.
- Observed Se release, esp. in neutral media.
- Consider environmental attenuation.



Continuing and Future Work

- **Evaluating links between released species.**
- **Examining release of halogens with metals.**
- **Continuing Integrated Framework Evaluation.**
- **Leaching gypsum and wallboard sample pairs.**

